

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
19 April 2001 (19.04.2001)

PCT

(10) International Publication Number
WO 01/27972 A2

(51) International Patent Classification⁷: **H01L**

(21) International Application Number: **PCT/US00/25518**

(22) International Filing Date:
18 September 2000 (18.09.2000)

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
60/154,716 20 September 1999 (20.09.1999) US
60/157,149 30 September 1999 (30.09.1999) US
09/527,885 20 March 2000 (20.03.2000) US
09/551,716 18 April 2000 (18.04.2000) US

(63) Related by continuation (CON) or continuation-in-part (CIP) to earlier applications:

US	60/157,149 (CON)
Filed on	30 September 1999 (30.09.1999)
US	09/551,716 (CON)
Filed on	18 April 2000 (18.04.2000)
US	09/527,885 (CON)
Filed on	20 March 2000 (20.03.2000)
US	60/154,716 (CON)
Filed on	20 September 1999 (20.09.1999)

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— Without international search report and to be republished upon receipt of that report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **MOLECULAR SCALE ELECTRONIC DEVICES**

(57) Abstract: Molecular scale electronic devices are disclosed. Such devices include at least two conductive contacts, and a conductive path bridging the contacts. The conductive path is able to be written into a perturbed state by a voltage pulse, which can be of high or low conductivity, relative to an initial state. The conductive path comprises organic molecules including at least one electron-withdrawing group. Room temperature negative differential resistance is exhibited by the devices.

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MOLECULAR SCALE ELECTRONIC DEVICES

Technical Field

This invention relates to electronic devices and methods of making them, and
5 more particularly to such devices and methods utilizing conductive organic materials.

Background

Chemically-assembled electronic devices can serve as extensions of
conventional circuits and devices. Such chemically-assembled devices include
nanoscale or molecular scale electronic components. Molecular scale systems can
10 offer distinct advantages in uniformity of structure and potentially lowered fabrication
costs. Additionally, these molecular components can offer the advantage of ease of
synthesis and the ability to create large varieties of structure by the use of facile
chemical transformations.

Summary

15 The invention is based on the fabrication of molecular scale electronic devices,
and the incorporation of such devices in useful circuits and components. The
molecular scale electronic devices include an active reduction-oxidation center, which
serves as a key element in the devices' exhibition of large negative differential
resistance (NDR), including room temperature NDR, large peak to valley ratios, and
20 switchable conductive states. The molecular scale electronic devices can operate as
memory devices by storing high or low conductivity states. The devices are
writeable, readable, and erasable.

In one aspect, the invention provides an electronic device including at least
two contacts, and a monolayer of conductive organic material forming a conductive
25 path between the contacts. The conductive path includes at least one electron
withdrawing group, which can be cyano, isocyano, nitro, sulfonyl, β -carboxyvinyl,
sulfinyl, β,β -dicyanovinyl, halogenated alkyl, formyl, carboxyl, carbonyl,
alkyloxycarbonyl and aryloxycarbonyl, 1-tetrazolyl, 5-chloro-1-tetrazolyl, carbamoyl,
or sulfamoyl, preferably cyano, isocyano and nitro. The device can exhibit high and

low conductivity states and can be made repeatedly switchable between the high and said low conductivity states. The low conductivity state can a current of less than about 100 pA or less than about 1 pA.

5 The high conductivity state can have a current at least about 200 times higher than the low conductivity state, preferably at least about 500 times higher than said low conductivity state, and more preferably at least about 1000 times higher than said low conductivity state. The electron withdrawing group can be bonded to a phenyl ring in the conductive path. At least one electron donating group can also be present in the conductive path.

10 The conductive path can include at least about 70% of its atoms being sp- or sp²-hybridized atoms and can include alternating ethynyl and aryl groups, or at least one phenyl-ethynyl linkage, with at least one of the phenyl groups substituted with an electron withdrawing group. The conductive path can further include binding groups which bind said conductive path to the contacts, for example, sulfur atoms, oxygen
15 atoms, cyano, carboxy, diazonium salt, halide, isocyano, phosphine, or tellurium and selenium atoms. The conductive path can include biphenyl groups, or ethenyl groups.

In another aspect, the invention provides an electronic device including two contacts, with at least one contact being a palladium contact; and a self-assembled monolayer of a conductive organic molecule including a phenyl-ethynyl-substituted
20 phenyl-ethynyl-phenyl linkage between the contacts, where the substituted phenyl includes at least one nitro group, and where the organic molecule is bonded to said palladium contact by at least one isocyano group on a terminal phenyl of said linkage.

In yet another aspect, the invention includes a memory circuit including an input, an output, a molecular electronic device, as described above, where one contact
25 of the device bridges the input and output, and where another contact of the device is at a low potential, or grounded, and a comparator also bridging the input and output, where the comparator is in electrical communication with a reference voltage. A memory array can be made, including a plurality of these memory circuits arranged in an addressable array.

In yet a further aspect, the invention provides a static random access memory cell including at least a first and a second molecular electronic device as described above, where the first device has one of its contacts connected to a reference voltage, and another of its contacts connected to a node, and where the other device has one of its contacts connected to a low potential or ground, and another of its contacts
5 connected to the node, and where the node is further connected to a low potential, or ground, and can also include a gain component.

The invention involves organic or organometallic molecules that store charge as a self-assembled nanoscale molecular device. The molecular devices form
10 electronically programmable and erasable memory bits. These bits are compatible with conventional threshold levels. The memory bits can be configured into memory cells applicable to random access memory devices. The molecular devices in such memory cells have long bit retention times (over ten minutes).

As used herein, "conjugation" or "conjugated groups" refers to an extended
15 system of overlapping π electrons on sp - and/or sp^2 -hybridized atoms. This results in overlapping π electron density not only within each pair of sp - and/or sp^2 -hybridized atoms, but between them as well.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to
20 which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described below. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety. In case of conflict, the present specification, including
25 definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

Other features and advantages of the invention will be apparent from the following detailed description, and from the claims.

Brief Description of the Drawings

Fig. 1 is a schematic diagram of a particular molecular device.

Fig. 2 is a closeup of the molecular device of Fig. 1, showing a pore formed in substrate and contact material.

5 Fig. 3 is a further closeup of the molecular device of Figs. 1 and 2, showing the molecules making up conductive paths between contacts.

Fig. 4 is a schematic diagram of a memory circuit utilizing a particular molecular device.

10 Fig. 5 is a schematic diagram of an SRAM cell using back-to-back negative differential resistance devices.

Fig. 6 is a schematic diagram of a basic SRAM circuit using back-to-back negative differential resistance devices with gain.

Fig. 7 is a schematic diagram of a basic SRAM circuit using back-to-back negative differential resistance devices without gain.

15 Fig. 8 is a plot of current vs. voltage for a particular molecular device.

Fig. 9 is a plot of current vs. voltage vs. temperature for a particular molecular device.

Fig. 10 is a plot of current vs. voltage for a particular molecular device, including initial and written states.

20 Fig. 11 is a plot of the difference between the initial and written states, described in Fig. 10.

Fig. 12 is a plot of bit retention measured as current vs. time, giving a bit retention time constant (τ).

25 Fig. 13 is a plot of the temperature dependence of τ giving an activation energy.

Fig. 14 is a plot of current vs. voltage of stored and initial/erased states for a particular molecular device at 60 K

Fig. 15 is a plot of current vs. voltage of stored and initial/erased states for a particular molecular device at 300 K.

Fig. 16 is a measured logic diagram demonstrating memory characteristics of a particular molecular device.

5 Fig. 17 is a plot of current vs. voltage for a particular molecular device at 300 K.

Fig. 18 is a plot of current vs. voltage for a particular molecular device at 190 K.

Fig. 19 is a cyclic voltammogram for a particular molecular device.

10 Fig. 20 is a cyclic voltammogram for a particular molecular device.

Detailed Description

The molecular scale electronic devices include metal contacts, and a monolayer of conductive organic material forming a conductive path between the contacts. Fig. 1 shows a particular embodiment of a molecular scale electronic device
15 1, including substrate 3, insulating material 5, and cavity 7. Cavity 7 is shown in greater detail in Fig. 2, which includes upper contact material 9 and lower contact material 11, and conductive path pore 13. Conductive path pore 13 is shown in greater detail in Fig. 3, which includes upper and lower contact material 9 and 11, respectively, as well as particular conductive path molecules 15.

20 Specific aspects of these devices are discussed in U.S. Provisional Applications Serial Nos. 60/157,149, filed September 30, 1999, and 60/154,716, filed September 20, 1999, each of which is hereby incorporated by reference in their entireties.

Conductive Path

25 Conductive organic material which is able to form a conductive path between metal contacts can be fabricated from substantially conjugated π -electron systems. Conductive paths are typically fabricated to have two "ends", each of which is in contact with a distinct contact. The lengths of such conductive paths can range from

about 5 to about 75 Å, preferably from about 10 to about 75 Å, and more preferably from about 10 to about 50 Å.

These π -electron systems can be fabricated using molecules with a number of sp^2 - and/or sp -hybridized carbon, nitrogen, sulfur, or oxygen atoms adjacent to each other, or separated by one, two consecutive, or less preferably three consecutive sp^3 -hybridized carbon, nitrogen, sulfur, or oxygen atoms. For example, conductive paths can be formed of from about 4 to about 40 atoms, of which a majority, or preferably at least about 70%, are sp^2 - or sp -hybridized. For example, conductive paths can comprise such all-carbon aromatic groups as phenyl, naphthyl, indyl, azulyl, pentaly, heptaly, biphenylenyl, indacenyl, acenaphthyl, fluorenyl, phenalenyl, phenanthrenyl, anthracenyl, triphenylenyl, pyrenyl, naphthacenyl, pentacenyl, hexacenyl, and the like; double-bond containing groups such as ethenyl, or 1,3-butadienyl; and triple bond containing groups such as ethynyl, or 1,3-butadiynyl. Conductive paths can also comprise heteroatom-containing groups such as pyridinyl, pyrazinyl, pyrazolyl, pyrrolyl, imidazolyl, thienyl, benzothienyl, naphthothienyl, thianthrenyl, furyl, pyranly, isobenzofuranyl, chromenyl, xanthenyl, phenoxathiinyl, pyrimidinyl, pyridaziny, indoliziny, isoindolyl, indolyl, purinyl, quinoliziny, quinolyl, phthalazinyl, pteridinyl, carbazolyl, acridinyl, phenanthridinyl, pyrrolinyl, imidazolinyl, indolinyl, and the like. Similarly, conductive paths can comprise combinations of the above groups, such as biphenyl, ethynyl-biphenyl-ethynyl, ethenyl-phenyl-ethenyl, pyridinyl-ethenyl-phenyl, phenyl-ethynyl-phenyl, ethynyl-phenyl-ethynyl, phenyl-ethynyl-phenyl-ethynyl, phenyl-ethynyl-phenyl-ethynyl-phenyl, phenyl-ethenyl-phenyl-ethenyl-phenyl, phenyl-ethenyl-biphenyl-ethenyl-phenyl, biphenyl-ethenyl-biphenyl, phenyl-ethynyl-biphenyl-ethynyl-phenyl, and many other possible combinations, which can be symmetric or asymmetric, regularly or irregularly alternating. Such groups can be arranged in branched or unbranched assemblies to form conductive paths. Conductive paths can also comprise organometallic groups such as chromium-arene groups.

Conductive paths also contain at least one, and optionally several, electron-withdrawing groups. Such groups stabilize radical anion states of organic molecules

comprising conductive paths. Such electron-withdrawing groups include cyano, isocyano, nitro, ammonium, sulfonyl (for example, octylsulfonyl, phenylsulfonyl, trifluoromethylsulfonyl, pentafluorophenylsulfinyl, and the like), β -carboxyvinyl, sulfinyl (for example, *t*-butylsulfinyl, trisulfinyl, trifluoromethylsulfinyl, pentafluorophenylsulfinyl, and the like), β,β -dicyanovinyl, halogenated alkyl (for example, trifluoromethyl, perfluorooctyl, ω -hydroperfluorododecyl, and the like), formyl, carboxyl, carbonyl (for example, acetyl, pivaloyl, benzoyl, trifluoroacetyl, and the like), alkyl- and aryloxy carbonyl (for example, ethoxycarbonyl, phenoxycarbonyl, and the like), 1-tetrazolyl, 5-chloro-1-tetrazolyl, carbamoyl (for example, dodecylcarbamoyl, phenylcarbamoyl, and the like), sulfamoyl (for example, trifluoromethylsulfamoyl, phenylsulfamoyl, ethylsulfamoyl, and the like). Preferred groups include nitro, nitrile and isocyano groups.

Such electron-withdrawing groups are bonded to, or in electronic communication with, atoms in the conductive path, or to atoms in conjugation with the conductive path. For example, an electron-withdrawing group can be directly bonded to phenyl, ethenyl, naphthyl, anthracyl, indolyl and the like, or can be bonded to a group such as an ethenyl or ethynyl group, which is in turn bonded to phenyl, naphthyl, anthracyl, indolyl, ethenyl and the like. The regiochemistry of such electron-withdrawing groups can influence the electronic characteristics. For example, variable regiochemistry of a nitro group on an aromatic ring system can exhibit differences in conduction properties between regioisomers. A single electron withdrawing group, or a number of electron withdrawing groups can be bonded to a single group such as a phenyl group, biphenyl group, pyridinyl group and the like.

Optionally, electron-donating groups can be bonded to, or in electronic communication with, atoms in the conductive path, or to atoms in conjugation with the conductive path. For example, an electron-donating group can be directly bonded to phenyl, naphthyl, anthracyl, indolyl, ethenyl and the like, or can be bonded to a group such as an ethenyl or ethynyl group, which is in turn bonded to phenyl, naphthyl, anthracyl, indolyl, ethenyl and the like. The regiochemistry of such electron-donating groups can influence the electronic characteristics. For example,

varying regiochemistry of an amine group on an aromatic ring system can exhibit differences in conduction properties between regioisomers.

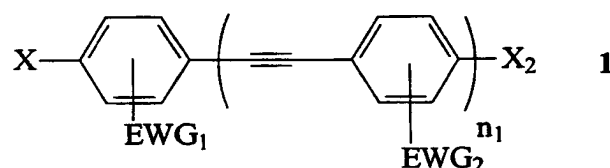
Suitable electron-donating groups include alkoxy, amine, hydroxy, thiol, and thioether. Alkoxy groups include those with a carbon chain of one to six carbons
5 containing an oxygen, which may contain one or more double or triple bonds, are straight or branched, and are optionally substituted with one or more halogen atoms. Included within the term alkoxy are methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, hexyloxy, heptoxy, and the like. Amine groups include primary, secondary and tertiary amine substituted with alkyl groups. Alkyl groups include
10 those with a carbon chain of one to six carbons, which may contain one or more double or triple bonds and are straight or branched, and optionally substituted with one or more halogen atoms. Included within the term alkyl are methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, cis-2-butene, trans-2-butene, hexyl, heptyl, and the like.

15 Conductive paths can optionally include barrier groups such as methylene ($-\text{CH}_2-$), or ethylene ($-\text{CH}_2-\text{CH}_2-$) groups; oxygen atoms; sulfur atoms; amine ($-\text{NR}-$) groups, where R is hydrogen, alkyl or substituted alkyl; azomethine ($-\text{N}=\text{CR}-$) groups, where R is hydrogen, alkyl or substituted alkyl; imine ($-\text{C}(=\text{NR})-$) groups, where R is hydrogen, alkyl or substituted alkyl; azo ($-\text{N}=\text{N}-$) groups; azoxy ($-\text{N}_2\text{O}-$) groups;
20 hydrazine ($-\text{NH}-\text{NH}-$) groups, and their alkyl substituted derivatives; amidine ($-\text{C}(=\text{NH})-\text{NH}-$) groups; carbodiimide ($-\text{N}=\text{C}=\text{N}-$) groups; guanidine ($-\text{NH}-\text{C}(\text{NH})=\text{N}-$) groups; urea ($-\text{NH}-\text{C}(=\text{O})-\text{NH}-$) or isourea ($-\text{N}=\text{C}(\text{OH})-\text{NH}-$) groups; and similar groups. These barrier groups can be interposed directly between the sp^2 - and/or sp -
25 hybridized atoms or groups mentioned above forming the conductive path. Such barrier groups can also be bonded to, and in electronic communication with, the conductive path, while not themselves forming part of the conductive path. Preferably, such barrier groups are limited in their incorporation in the conductive path, so as not to unduly limit the conductivity of the path. On the other hand, selective incorporation of such non- sp - or sp^2 -hybridized barrier groups can be used to

fine-tune the conductivity of the path. Electron-withdrawing groups and/or electron-donating groups can be included on either side, or both sides, of barrier groups.

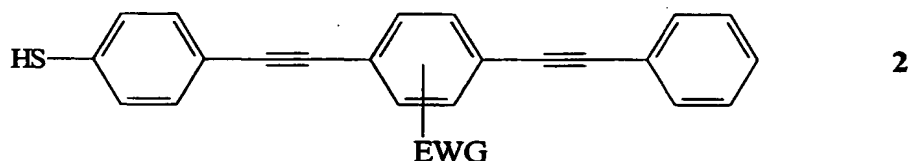
In particular examples, suitable conductive paths can include the organic compounds represented by phenylene ethynylenes, such as following general structure

5 1.



where X and X₂ are independently selected, and can be thiol or other sulfur-containing group such as thioacetyl, isocyano, cyano, carboxy, diazonium salt, phosphine, halide or hydrogen atoms or group VIb atoms such as tellurium, selenium, and other chalcogens; and where n₁ is an integer from 1 to 5, and if n₁ is zero, the conductive path includes a substituted phenyl ring and a binding group. EWG₁ is optionally present if n₁ is greater than 1. At least one of EWG₁ and EWG₂ is present in the conductive path. EWG₂ can be different for different phenyl rings within n₁, if n₁ is greater than 1. EWG₁ and EWG₂ are independently selected, and can be cyano, isocyano, nitro, sulfonyl (for example, octylsulfonyl, phenylsulfonyl, trifluoromethylsulfonyl, pentafluorophenylsulfinyl, and the like), β-carboxyvinyl, sulfinyl (for example, *t*-butylsulfinyl, trisulfinyl, trifluoromethylsulfinyl, pentafluorophenylsulfinyl, and the like), β,β-dicyanovinyl, halogenated alkyl (for example, trifluoromethyl, perfluorooctyl, ω-hydroperfluorododecyl, and the like), formyl, carboxyl, carbonyl (for example, acetyl, pivaloyl, benzoyl, trifluoroacetyl, and the like), alkyl- and aryloxy carbonyl (for example, ethoxycarbonyl, phenoxycarbonyl, and the like), 1-tetrazolyl, 5-chloro-1-tetrazolyl, carbamoyl (for example, dodecylcarbamoyl, phenylcarbamoyl, and the like), sulfamoyl (for example, trifluoromethylsulfamoyl, phenylsulfamoyl, ethylsulfamoyl, and the like).

A suitable example of the general structure 1 is presented by structure 2, in which EWG is described as above for either EWG₁ or EWG₂.



5

Any of these molecules can be substituted, as will be detailed below.

Additional linkages can be introduced between any of the phenyl rings, or on any of the terminal phenyl rings, including methylene, ethylene, propylene and other non-sp- or sp²-hybridized atoms. Conduction barriers such as, for example, alkyl groups, can be positioned in the conductive path to disrupt the electronic characteristics of molecular devices. For example, resonant tunneling diodes can be fabricated utilizing such altered electronic characteristics. Conductive paths can be synthesized that have no barriers, one or more barriers, two contacts, or more contacts, or any combination of such features.

The end groups shown in the above structure 1 (that is, X and X₂) are binding groups that allow attachment to contact material described above. The binding groups can be thiol or other sulfur-containing group such as thioacetyl, isocyano, cyano, carboxy, diazonium salt, phosphine, halide or hydrogen atoms or group VIb atoms such as tellurium, selenium, and other chalcogens. Preferably, not all such binding groups are hydrogen atoms. In some cases, it is believed that expulsion of the X or X₂ group occurs upon formation of the conductive path monolayer. For example, if a diazonium salt-containing conductive path is utilized, nitrogen gas can be released upon formation of the conductive path monolayer. If a halide-containing conductive path is utilized, the halogen atom can be expelled upon formation of the conductive path monolayer.

Binding groups can be tailored to optimize the overlap between the lowest unoccupied molecular orbital (LUMO) or the conductive path molecule, and the Fermi levels of the contact material. Covalent, ionic, or other non-covalent interactions can be involved between conductive paths and the contact. In such cases, groups such as hydrogen atoms will be the conductive path atoms nearest the contact. Some embodiments can involve conductive paths in the form of Langmuir-Blodgett films, and therefore such embodiments do not require groups which covalently bond either end of the conductive path to the contact.

The synthesis of such conductive paths can include the synthesis of groups that mask binding groups. For example, thioacetyls represent protected thiols that act as binding sites for the conductive paths to a contact surface. In such instances, removal of the acetyl protecting groups with sodium hydroxide in aqueous tetrahydrofuran and rapid workup can produce thiol groups. Alternately and preferably, ammonium hydroxide can be provided *in situ* for removal of acetyl groups.

In some preferred embodiments, either one or two of such binding groups can be incorporated into conductive paths. It is also possible for a conductive path to include more than one such binding group on one end of a conductive path.

The monolayers are desirably arranged as assemblies of molecules, occupying the surface of a contact. The assemblies can range from several hundred thousand to several molecules, to the limit of a single molecule. The contact surface area covered by such assemblies are of the nanoscale size range. That is, from about 1 to about 200 nm in diameter. Preferably, the assemblies cover contact surface with diameters from about 1 to about 50 nm. The contact surface area covered by multi-molecule assemblies are typically of roughly circular or oval shape, although other arrangements are also possible, such as square, or rectangular with substantially equal or substantially unequal side lengths. The assemblies can be present in a regular array or an irregular arrangement on the contact surface. Preferably, the arrangement of monolayer assemblies is substantially regular, as suits typical applications such as random access memory devices. For example, assemblies can be arranged every few

hundred nanometers, or every few microns, up to every few millimeters. Preferably, the space between assemblies will be as small as possible to maximize the use of space on the contact or substrate surface.

5 Contacts

The devices of the invention include at least two contacts. To each end of the conductive path described above, a contact is made, either by a covalent bond, by an ionic bond, or by through-space interaction with the conductive path.

10 The contacts are made of any highly conductive material or conductive material with a thin (less than about 10 Angstroms) insulating, that is, oxide layer. Metal contacts can be used, and any metal is suitable, particularly those commonly used in electronics, such as copper, gold, palladium, titanium, silver, and the like. The metal is preferably of moderate smoothness, but can otherwise be of any useful topology or surface geometry. The contacts need not be pure metal. For example, the
15 contacts can be surfaces of highly conductive material deposited across at least a portion of a material of lesser conductivity. In the fabrication of such contacts, any suitable conventional method can be used to create metal contacts that can readily be equipped with electrical contacts. For example, metal can be deposited on a substrate such as a silicon wafer, for example, by a method such as thermal evaporation,
20 sputtering, laser assisted deposition techniques, or chemical deposition techniques. Typically, an insulating layer such as silicon nitride, or silicon oxide is then deposited on the metal surface, by methods known in the art. The insulating layer can then be selectively removed in locations in which it is desired to establish molecular scale electronic devices. The removal of insulating material can be carried out, for
25 example, by photolithography, or other known methods. Such a prepared contact is then ready for self-assembled monolayer formation, Langmuir Blodgett film formation, or other method of establishing a monolayer of conductive material. Particular examples of such methods will be detailed below.

30 The conductive paths are disposed on the contact in the form of an ordered monolayer. Preferably, the density of the monolayer is comparatively high.

That is, given the possible number of sites on the contact available for conductive path molecules to bind, as many of such sites as possible will be occupied by the molecules. One method of providing such an ordered monolayer is by a self-assembled monolayer (SAM) method. Such methods for providing well-defined, stable and reproducible metallic contacts to self-assembled monolayers of conductive paths are demonstrated, for example, in Zhou et al., *Appl. Phys. Lett.* 71, (1997) 611-613, which is hereby incorporated by reference in its entirety.

Another way of providing monolayers of conductive paths is by formation of a Langmuir-Blodgett (L-B) film. Such a film can be constructed by transferring mono-layers of conductive paths, floating on a liquid surface to a solid substrate. In such films, the thickness and molecular arrangement of the film can be controlled at the molecular level. Such films generally require conductive paths having hydrophilic and hydrophobic ends. For example, a molecule with a hydrophilic group such as a carboxylic acid, and a hydrophobic group such as a C₅-C₁₅ alkyl group can be synthesized.

After deposition of the SAM or L-B film, a layer of contact material is deposited on the top of the SAM. The methods of Zhou et al. are designed to ensure that the deposition of metal atoms accumulate at the SAM surface, and do not penetrate into the organic layer. The material constituting the contact layer on top of the SAM can be the same or different than that on which the SAM is deposited.

The contacts can be of any convenient shape. For some applications, wafers of silicon coated with metal can be used. The metal contacts can be surfaces that are substantially parallel to each other.

Synthesis of Conductive Paths

The class of conductive paths represented by general structure 1 can be synthesized according to a general synthetic procedure as follows. A dihalobenzene, which can be further substituted with electron withdrawing groups or optionally additional electron donating groups can be used as a starting material. For example,

the starting material can be a molecule such as *p*-bromiodobenzene, or 2-bromo-5-iodo-nitrobenzene. This material can be monocoupled to a triaryl- or trialkylsilylacetylene using a method such as the Sonagashura coupling procedure. The product of this reaction can then be coupled to an electron withdrawing group- or
5 electron-donating group-substituted or unsubstituted phenylacetylene using the same coupling reagents, but a higher temperature. Terminal silyl protection can be removed with typical reagents such as potassium carbonate, and the product reacted with a haloaryl group including a masked or unmasked binding group. This haloaryl group can also include electron withdrawing groups and/or electron donating groups.
10 For example, this haloaryl group can be a halothioacetylbenzene, such as *p*-iodothioacetylbenzene.

Conductive paths including biphenyl groups can be constructed analogously, by dihalogenating, for example, 4,4'-dibrominating, a substituted or unsubstituted biphenyl group. For example, a 2,2'-dinitro- or 2,2'-dicyanobiphenyl
15 can be used as a starting material. Such material can be coupled to trialkylsilylacetylene at 4- and 4'-positions of the biphenyl ring. The terminal acetylenes can be revealed and coupled to haloaryl groups by the general methods described herein. The haloaryl groups can further comprise masked or unmasked binding groups.

20 Such synthetic strategies are applicable to a wide variety of aryl groups, including heteroaromatic structures. For example, electron withdrawing group-substituted bipyridinyl groups can be used as starting materials by coupling pairs of nitro-halo-pyridine with copper reagents. Halogenation of the resulting dimer gives a product which can be used in the above described coupling procedures.

Properties of the Devices

The molecular devices described herein have useful electronic properties. For example, they can exhibit negative differential resistance and this property can be observed at temperatures of up to 300 K at least. Their current vs. voltage, $I(V)$,
30 curves can exhibit non-linear behavior. The molecular devices described herein can

store high or low conductivity states, and therefore function as static or dynamic random access memories.

The molecular devices described herein can exhibit memory effects. The electronic devices act as a memory device by the storage of a high or low conductivity state. The initial state is written into a perturbed state upon the application of a voltage pulse. The perturbed state persists as a stored bit, which is not changed by successive read pulses, which are also voltage pulses. Compounds with electron-withdrawing groups proximally bonded to the conductive path change their conductivity state. Other substituents can be provided in or proximate the conductive path, including electron-donating groups.

The initial state can be either a high conductivity or a low conductivity state. For example, a molecular device including a conductive path having both an electron-withdrawing group such as, for example, nitro, and an electron-donating group, such as, for example, acetamido or amino has an initial state which is a low conductivity state. Application of a voltage pulse converts this initial state into a high conductivity state, which persists, and is unaffected by subsequent voltage pulses of the same polarity, which can serve to read the state of the device. As another example, a molecular device can be prepared including a conductive path with an electron-withdrawing group such as nitro, and no electron-donating group present. While not wishing to be bound by any particular theory of operation, such a device appears to be reduced relatively readily upon application of a low potential, resulting in an apparent initial state, which is a high conductivity state. Application of a standard voltage pulse converts this apparent initial state into a low conductivity state which persists for a long time period.

For a device having current density of 50 A/cm^2 , the low conductivity state can have a peak current of from about 50 pA to less than about 1 pA. For the same type of device, the high conductivity state can have a peak current of from about 1 nA to about 100 nA. Such devices thus exhibit on-off ratios in conductivity from about 200 to about 1000. This value is temperature dependent, and can be as high as about 1000 at 260K.

Electronic Devices Utilizing Molecular Scale Devices

The molecular devices can be incorporated into electronic devices such as memory circuits, SRAM circuits as described herein.

5 A memory circuit utilizing a programmable molecular scale device is shown in Fig. 4. The figure shows memory circuit 21 including input 23, output 25 and ground 27. Memory element 29 is a molecular scale electronic device as described herein, with leads 31 and 33 connected to contacts 35 and 37, respectively. Switches 39, 41, 43 and 44 can be, for example, field effect transistors, that are
10 controlled by address decoding circuitry, shown as toggles for simplicity. Amplifiers 45 and 47 are optional, depending on the resistance of the memory element 29. If its resistance is high, amplification can be found to be necessary. Comparator 49 is shown, also having V_{ref} 51.

 To write data in the memory, switches 39 and 41 are closed, thereby
15 connecting memory element 29 to the input data through the amplifier 45. The switches are then opened. To read data from memory, the output switch 43 is closed to connect the memory element 29 to comparator 49, which “decides” whether the stored state is less than or greater than reference voltage 51. The output of comparator 49 is a logic “0” or a logic “1”, depending on this result. To reset the
20 memory state, switches 41 and 44 are closed.

 This circuit can be employed in a memory array, according to methods and architectures known to those of skill in the art. For example, input and output can be separately connected to chip surfaces to define a grid system. Thus, the address of each memory circuit is unique.

25 The molecular scale devices can also be included in static random access memory (SRAM) as described herein. Fig. 5 shows an SRAM circuit that can be made from molecular scale devices. SRAM cell 60 includes negative differential resistance devices 61 and 63, each of which is a molecular scale device as described herein. The RTD can be the same or of different composition. The two NDR devices

are connected in back-to-back relationship with each other between a positive supply voltage V_{ref} and ground. This produces a circuit that exhibits bistable operation. The I-V characteristics of each of the two NDR devices is plotted in Fig. 5, in which the dashed curve is for NDR1 and the solid curve terminating at $(V_{ref}, 0)$ is for NDR2. As indicated in Fig. 5, the two devices connected in that way have two stable operating points, namely, the two points at which the two curves intersect, one above the NDR region and one below the NDR region. If there is an excess leakage current, $I_{leakage}$, at node SN, then one of the curves will be displaced upward as shown.

Switching from one stable point to the other is produced by supplying negative or positive current to node SN. If the current drawn out of node SN is sufficiently large, that will cause the circuit to switch from $V_{SN_{high}}$ to $V_{SN_{low}}$, where $V_{SN_{high}} > V_{SN_{low}}$. Conversely, if the current supplied to node SN is sufficiently large, that will cause the circuit to switch from $V_{SN_{low}}$ to $V_{SN_{high}}$.

The circuit of Fig. 6 shows an embodiment of a basic SRAM cell in which the switching current is supplied by a write FET 70. The signal on word line 72 causes write FET 70 to write the signal on bit line 74 into the bistable circuit, thereby setting the voltage at node SN. The voltage at node SN, in turn, drives the gate of a read FET 76. Read FET 76, which has another FET 78 serving as its load, is either on or off, depending upon the voltage at node SN. When on, the voltage at V_{out} will be high and when off, the voltage at V_{out} will be low.

The circuit of Fig. 7 shows a simpler SRAM cell in which the read out circuit of Fig.6 is replaced by a simple capacitor.

The invention will be further described in the following examples, which do not limit the scope of the invention described in the claims.

Examples

The following examples illustrate certain advantages and properties of particular embodiments of molecular devices and methods of making them. Certain general procedures will be described initially, followed by specific examples.

Example 1: General Conditions.

All reactions were performed under an atmosphere of nitrogen unless stated otherwise. Alkyl lithium reagents were obtained from FMC Corporation (Chicago, IL). Pyridine, methyl iodide, triethylamine, and N,N-dimethylformamide (DMF) were distilled over calcium hydride, and stored over 4 Å molecular sieves. Toluene and benzene were distilled over CaH₂. Methylene chloride and hexanes were distilled. Ethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. Triethylamine and N, N-diisopropylethylamine were distilled over calcium hydride. Methanol (MeOH) was dried over oven dried 3 Å molecular sieves. ¹H NMR spectra were recorded at 300, 400, or 500 MHz on Brüker AM-300, WH-400, and AM-500 spectrometers, respectively or at 400 and 500 MHz on Varian Mercury 400 and INOVA 500 spectrometers, respectively. The ¹³C NMR spectra were recorded at 75, 100, or 125 MHz on Brüker AM-300, WH-400, and AM-500 spectrometers, respectively at 100 and 125 MHz on Varian Mercury 400 and INOVA 500 spectrometers, respectively. Proton chemical shifts (δ) are reported in ppm downfield from tetramethylsilane (TMS) and ¹³C resonances (unless otherwise noted) were recorded using the 77.0-ppm CDCl₃ resonance as an internal reference and are reported in ppm downfield from TMS. Infrared (IR) spectra were recorded on a Perkin Elmer 1600 Series FTIR. Gas chromatography experiments were performed on a Hewlett-Packard GC model 5890A equipped with an Alltech column (cat # 932525, serial # 9059) 25 m × 0.25 mm D × 0.2 mm. Gravity column chromatography, silica gel plugs, and flash chromatography were performed using 230-400 mesh silica gel from EM Science. Thin layer chromatography was performed using glass plates precoated with silica gel 60 F₂₅₄ with a layer thickness of 0.25 mm purchased from EM Science. Combustion analyses were obtained from Atlantic Microlab, Inc., P. O. Box 2288, Norcross, GA 30091.

Example 2: General Procedure for Coupling Terminal Alkynes with ArylHalide

The general procedure for coupling terminal alkynes with aryl halides utilizes a palladium-copper cross-coupling protocol known as the Castro-

- 5 Stephens/Sonogashira Protocol (Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tet. Lett.* (1975), 4467. Stephens, R. D.; Castro, C. E. *J. Org. Chem.* (1963), 28, 3313. Suffert, J.; Ziessel, R. *Tetrahedron Lett.* (1991), 32, 757. Blum, J.; Baidossi, W.; Badreih, Y.; Hoffmann, R. E.; Shumann, H. *J. Org. Chem.* (1995), 60, 4738).

- To an oven dried round bottom flask equipped with a water cooled West
10 condenser or screw capped pressure tube with a magnetic stirbar were added the aryl halide, bis(triphenylphosphine)palladium(II) dichloride (3-5 mol % per halide), and copper(I) iodide (6-10 mol % per halide). Triphenylphosphine was used in some reactions to keep the palladium in solution. The vessel was then sealed with a rubber septum under a N₂ atmosphere. A co-solvent system of THF, benzene, or methylene
15 chloride was added at this point depending on the solubility of the aryl halide. Then base, either triethylamine or N,N-diisopropylethylamine, was added and finally the terminal alkyne (1-1.5 mol % per halide) was added and the reaction was heated until complete. Upon completion of the reaction, the reaction mixture was then quenched with water, a saturated solution of NH₄Cl, or brine. The organic layer was diluted
20 with methylene chloride or Et₂O and washed with water, a saturated solution of NH₄Cl, or brine (3×). The combined aqueous layers were extracted with methylene chloride or Et₂O (2×). The combined organic layers were dried over MgSO₄ and solvent removed *in vacuo* to afford the crude product that was purified by column chromatography (silica gel). Eluents and other slight modifications are described
25 below for each material.

Example 3: General procedure for Deprotection of Trialkylsilyl-Protected Alkynes.

- Two general methods were carried out for the deprotection of trialkylsilyl-protected alkynes. According to the first method, the silylated alkyne
30 was dissolved in methanol and potassium carbonate was added. The mixture was

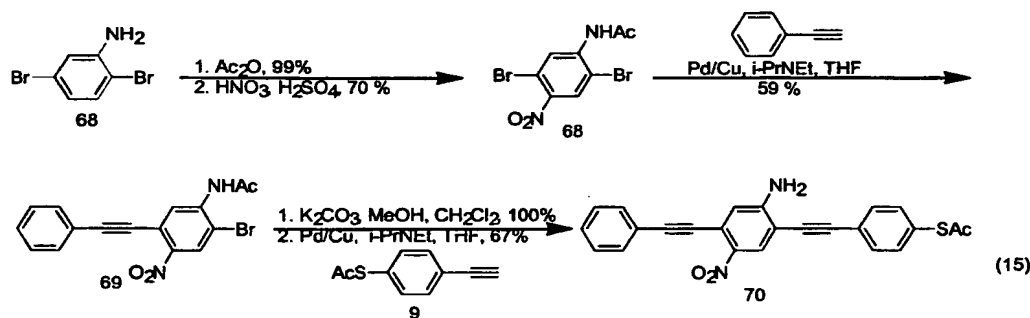
stirred overnight before poured into water. The solution was extracted with ether or ethyl acetate and washed with brine. After drying over magnesium sulfate the solvent was evaporated *in vacuo* to afford pure products. According to the second method, the silylated alkyne was dissolved in pyridine in a plastic vessel. A mixed solution of
5 49% hydrofluoric acid and 1.0 M tetrabutylammonium fluoride in THF was added at room temperature. The solution was stirred for 15 min and quenched with silica gel. The mixture was poured into water and extracted with ether. The extract was washed with brine and dried over magnesium sulfate. After filtration the solvent was evaporated *in vacuo*. The crude products were purified by a flash chromatography on
10 silica gel. Eluents and other slight modifications are described below for each material.

Example 4: General procedure for Conversion of Aryl Halide to Arylthioacetate.

15 To *t*-BuLi (2 equiv. per halide) in ether (5 mL) at -78 °C was added a solution of the aryl halide in THF. The slurry was stirred for 40 min and a slurry of sulfur powder (0.26 g, 8.0 mmol) in THF (10 mL) was added via cannula. The resulting green slurry was stirred for 1 h and then warmed to 0 °C. The mixture was recooled to -78 °C and acetyl chloride (1.2 equiv. per halide) was added. The resultant yellow
20 solution was allowed to warm to room temperature and stirred for 1 h before quenching with water. The mixture was extracted with ether (3 ×). The combined organic fractions were washed with water (2 ×) and dried over magnesium sulfate. Removal of solvents *in vacuo* followed by flash chromatography afforded the desired material. Eluents and other slight modifications are described below for each
25 material.

Example 5: Synthesis of 2'-amino-4,4'-diphenylethynyl-5'-nitro-1-thioacetylbenzene

The synthesis of a functionalized conductive path useful for constructing a molecular scale device is described below. The general synthetic procedure is presented in the following scheme:



5

To synthesize the starting material, 2,5-dibromoacetanilide; to a 500 mL round bottom flask equipped with a magnetic stirring bar and a West condenser were added 2,5-dibromoaniline (1.38 g, 55.0 mmol), acetic anhydride (50 mL), and water (50 mL). The reaction mixture was allowed to heat to reflux for 12 h. The resultant mixture was cooled to ambient temperature and poured into water (500 mL). The precipitate was collected by filtration and further washed by water. The reaction afforded 14.25 g (88 % yield) of 2,5-dibromoacetanilide.

To synthesize 2,5-dibromo-4-nitroacetanilide; to a oven dried 500 mL round bottom flask equipped with a magnetic stirring bar were added sulfuric acid (50 mL), and nitric acid (50 mL) and the reaction mixture was cooled to 0 °C. Caution must be exercised during the synthesis of this compound to ensure that multiple nitrations are not carried out on the ring, which may lead to explosive, polynitrated compounds. 2,5-Dibromoacetanilide (14.25 g, 48.65 mmol) was added and the reaction mixture was allowed to stir for 2.5 h. Upon completion, ice (300 g) was added slowly to the reaction mixture. The reaction mixture was filtered and the solid collected. The desired material was purified by flash liquid chromatography using silica gel as the stationary phase and methylene chloride as the eluent. The reaction afforded 11.27 g (69 % yield) of 2,5-dibromo-4-nitroacetanilide.

To synthesize 2-bromo-4-nitro-5-(phenylethynyl)acetanilide; the general procedure for the Pd/Cu-catalyzed coupling reaction was used. 2,5-Dibromo-4-nitroacetanilide (3.0 g, 8.88 mmol) was coupled to phenylacetylene (0.98 mL, 8.88 mmol) as described above using copper(I) iodide (0.17 g, 0.89 mmol),
5 bis(triphenylphosphine)palladium(II) chloride (0.25 g, 0.44 mmol), triphenylphosphine (0.47 g, 1.78 mmol), N,N-diisopropylethylamine (6.18 mL, 35.52 mmol), and THF (25 mL) in an oven dried round bottom flask equipped with a West condenser and a magnetic stirring bar. The reaction mixture was allowed to react at room temperature for 1 d then was heated to 50 °C for 12 h. The resultant mixture
10 was subjected to an aqueous workup as described above. The 2-bromo-4-nitro-5-(phenylethynyl)acetanilide was purified by gravity liquid chromatography using silica gel as the stationary phase and methylene chloride as the eluent. The reaction afforded 1.79 g (56% yield, first crop) of the desired product.

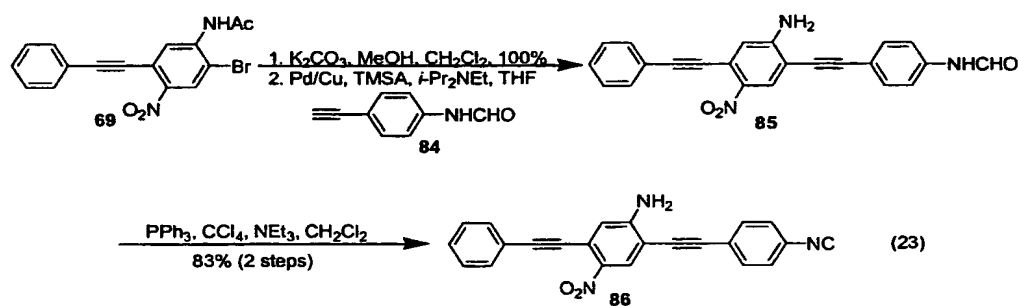
To synthesize 2-bromo-4-nitro-5-(phenylethynyl)aniline; the general
15 procedure for the deprotection of trimethylsilyl-protected alkynes was used. To a 100 mL round bottom flask equipped with a magnetic stirbar 2-bromo-4-nitro-5-(phenylethynyl)acetanilide (0.33 g, 0.92 mmol), potassium carbonate (0.64 g, 4.6 mmol), methanol (15 mL), and methylene chloride (15 mL) was added. The reaction was allowed to stir at room temperature for 1 h. The reaction mixture was quenched
20 with water and extracted with methylene chloride (3 ×). The organic layers were combined and dried over magnesium carbonate. Solvents were removed *in vacuo*. No further purification needed. The reaction afforded 0.29 g (100% yield) of 2-bromo-4-nitro-5-(phenylethynyl)aniline as a yellow solid.

To synthesize 2'-amino-4,4'-diphenylethynyl-5'-nitro-1-thioacetylbenzene;
25 the general procedure for the Pd/Cu-catalyzed coupling reaction was used. 2-Bromo-4-nitro-5-(phenylethynyl)aniline (0.10 g, 0.30 mmol) was coupled to 1-thioacetyl-4-ethynylbenzene (0.10 g, 0.56 mmol) as described above using copper(I) iodide (0.01 g, 0.03 mmol), bis(triphenylphosphine)palladium(II) chloride (0.01 g, 0.02 mmol), triphenylphosphine (0.02 g, 0.06 mmol), N,N-diisopropylethylamine (0.24 mL, 1.40
30 mmol), and THF (10 mL) in an oven dried round screw capped pressure tube

equipped with a stirring bar. The reaction mixture was allowed to react at 80 °C for 3 d. The resultant mixture was subjected to an aqueous workup as described above. The 2'-amino-4,4'-diphenylethynyl-5'-nitro-1-thioacetylbenzene was purified by gravity liquid chromatography using silica gel as the stationary phase and 3:1 methylene chloride/hexanes as the eluent. An additional hexanes wash gave pure yellow crystals of 2'-amino-4,4'-diphenylethynyl-5'-nitro-1-thioacetylbenzene, 0.80 g (67 % yield).

Example 6: Synthesis of 2'-Amino-4,4'-diphenylethynyl-5'-nitrobenzenisonitrile

A molecular scale device with an isonitrile attachment moiety was synthesized according to the scheme below. The starting material was prepared as described in Example 5. The amine moiety in intermediate 69 (2-bromo-4-nitro-5-(phenylethynyl)acetanilide) was unmasked with potassium carbonate and methanol, followed by Pd/Cu-catalyzed cross coupling with the formamide bearing compound 84 to afford compound 85 (2'-amino-4,4'-diphenylethynyl-1-formamido-5'-nitrobenzene). This intermediate was found to be insoluble in most solvent systems and therefore used directly in the next reaction.



The formamide was dehydrated in the presence of carbon tetrachloride, triphenylphosphine, triethylamine, and methylene chloride to afford molecular scale

device 2'-amino-4,4'-diphenylethynyl-5'-nitrobenzenisonitrile. The detailed synthesis is presented below.

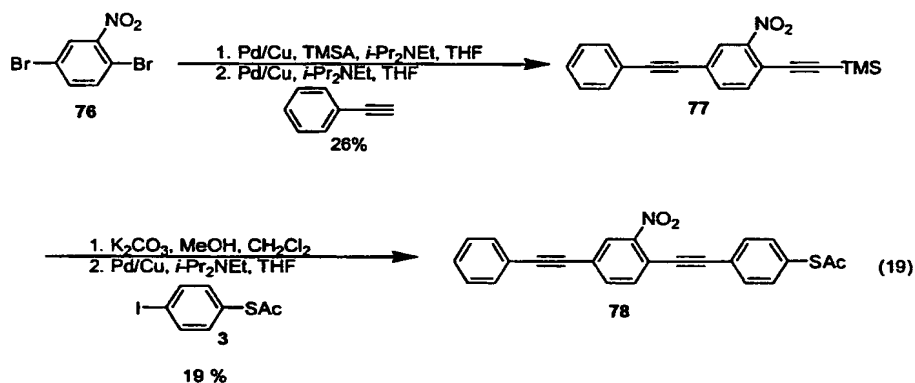
The intermediate 69 (2-bromo-4-nitro-5-(phenylethynyl)acetanilide) was synthesized as in Example 5. To synthesize 2'-amino-4,4'-diphenylethynyl-1-formamido-5'-nitrobenzene; the general procedure for the Pd/Cu-catalyzed coupling reaction was used. 2-Bromo-4-ethynylphenyl-5-nitroaniline (69) (0.26 g, 0.83 mmol) was coupled to 1-ethynyl-4-formamidobenzene (85) (0.15 g, 1.00 mmol) as described above using copper(I) iodide (0.02 g, 0.08 mmol), bis(triphenylphosphine)palladium(II) chloride (0.03 g, 0.04 mmol), N,N-diisopropylethylamine (0.58 mL, 3.32 mmol), and THF (25 mL) in a screw capped pressure tube equipped with a magnetic stirring bar. The reaction mixture was allowed to stir at 70 °C for 3 days. The resultant mixture was subjected to an aqueous workup as described above. The 2'-amino-4,4'-diphenylethynyl-1-formamido-5'-nitrobenzene was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:1 ethyl acetate/hexanes as the eluent. An additional purification was performed using gravity liquid chromatography using silica gel as the stationary phase and a mixture of ethyl acetate as the eluent. The reaction afforded an impure product of 0.23 g. The crude reaction product was taken on to the next synthetic step.

To synthesize 2'-amino-4,4'-diphenylethynyl-5'-nitrobenzenisonitrile (86); to an oven dried 100 mL round bottom flask equipped with a stirbar and a West condensor 2'-amino-4,4'-diphenylethynyl-1-formamido-5'-nitrobenzene (85) (0.04, 0.10 mmol), triphenylphosphine (0.09 g, 0.33 mmol), triethylamine (0.04 mL, 0.39 mmol), carbontetrachloride (0.03 mL, 0.31 mmol), and methylene chloride (10 mL) were added. The reaction was heated to 60 °C for 5 h. The reaction mixture was cooled and quenched with water and extracted with methylene chloride (3×). Organic layers were combined and dried over MgSO₄. Volatiles were removed *in vacuo*. The crude reaction mixture was purified by gravity liquid chromatography using silica gel as the stationary phase and ethyl acetate as the eluent. An additional purification was performed using gravity liquid chromatography using silica gel as the stationary phase

and a mixture of 1:1 methylene chloride/hexanes as the eluent. The reaction afforded 0.03 g (83 % yield, 2 steps) of 2'-amino-4,4'-diphenylethynyl-5'-nitrobenzenisonitrile.

5 Example 7: Synthesis of 4-(4'-(phenylethynyl)-2'-nitro-1'-(ethynyl)phenyl)-1-(thioacetyl)benzene

To determine the effects of an electron withdrawing moiety on electrical properties of these compounds, materials with solely a nitro moiety was synthesized.



10

2,5-Dibromonitrobenzene was subsequently Pd/Cu catalyzed with trimethylsilylacetylene to the more reactive bromide, ortho to the nitro moiety, and then to phenylacetylene that afforded intermediate (77). Deprotection of the terminal acetylene followed by coupling to the 1-iodo-4-thioacetylbenzene (3) afforded molecular scale device (78). A detailed synthetic procedure follows.

15

To synthesize 1-Bromo-3-nitro-4-(trimethylsilylethynyl)benzene; the general procedure for the Pd/Cu catalyzed coupling reaction was used. 2,5-dibromo-nitrobenzene (1.37 g, 4.89 mmol), bis(triphenylphosphine) palladium (II) chloride (0.17 g, 0.25 mmol), copper (I) iodide (0.09g, 0.49 mmol), and a stirbar were added to an oven-dried large screw cap tube. Air was removed and nitrogen backfilled (3×). THF (30 mL), Hünig's base (3.41 mL, 19.56 mmol), and trimethylsilylacetylene (0.69 mL, 4.9 mmol) were then added via syringe under nitrogen. The tube was capped and heated to 70 °C in an oil bath. After 18 h, the reaction flask was cooled to room

20

temperature and quenched with NH_4Cl solution. The organic products were extracted using NH_4Cl solution and methylene chloride. Due to difficulty in separation of products, full isolation was not achieved and the resulting mixture was carried on to the next reaction step.

5 To synthesize 1-nitro-2-(trimethylsilylethynyl)-5-(phenylethynyl)benzene; the general procedure for the Pd/Cu catalyzed coupling reaction was used. Bis(triphenylphosphine) palladium (II) chloride (0.14 g, 0.20 mmol), copper (I) iodide (0.07 g, 0.40 mol), and a stir bar were added to an oven dried, large screw cap tube. The reaction mixture from the previous reaction was placed in a small flask and air
10 removed and nitrogen backfilled (3 \times). Distilled THF was used to dissolve the mixture in the flask while under nitrogen and the resulting solution was transferred via syringe to the screw cap tube. Hünig's base (2.79 mL, 16.0 mmol) and phenylacetylene (0.57 mL, 5.2 mmol) were then added via syringe to the screw cap tube. The tube was capped and heated to 70 °C in an oil bath. After 3 d, the reaction tube was cooled to
15 room temperature and quenched with NH_4Cl solution and extracted with methylene chloride to afford a thick red-brown oil. Column chromatography (silica gel with 2:1 hexanes/ methylene chloride as eluent) afforded the desired product (0.172 g, 26 % yield).

 To synthesize 1-nitro-2-(ethynyl)-5-(phenylethynyl)benzene; the general
20 procedure for the deprotection of a trimethylsilyl-protected alkyne was used. 1-nitro-2-(trimethylsilylethynyl)-5-(phenylethynyl)benzene (0.17 g, 0.53 mmol) was deprotected to the terminal alkyne via the procedure described above using potassium carbonate (0.36 g, 2.6 mmol), methanol (10 mL), and methylene chloride (10 mL). The mixture, in a round bottom flask, was stirred at room temperature for 2 hours.
25 Extraction of the product followed the procedure described previously to yield 0.128 g of the desired product which was immediately reacted in the next step.

 To synthesize 4-(4'-(phenylethynyl)-2'-nitro-1'-(ethynyl)phenyl)-1-(thioacetyl)benzene; the general procedure for the Pd/Cu catalyzed coupling reaction was used. 1-nitro-2-(ethynyl)-5-(phenylethynyl)benzene (0.13 g) was coupled with 4-
30 thioacetyl-iodobenzene (0.19 g, 0.68 mmol) using the Pd/Cu cross coupling method

described earlier using bis(triphenylphosphine) palladium (II) chloride (0.019 g, 0.026 mmol), copper (I) iodide (0.01 g, 0.05 mmol), THF (30 mL), and Hünig's base (0.367 mL, 2.10 mmol) in an oven dried screw cap tube under nitrogen. The tube was stirred in a 60 °C oil bath for 23 h. The tube was then cooled to room temperature and quenched and extracted as stated before. Column chromatography (silica gel with 1:1 hexanes/ methylene chloride as eluent) afforded the desired product (0.040 g, 18.8% yield over two steps) as a yellow solid.

Example 7: I(V) Characteristics of Molecular Electronic Devices

Negative differential resistance (NDR) was investigated for particular molecular devices described herein.

The starting substrate for the device fabrication was a 250 μm thick double side polished silicon (100) wafer, upon which 50 nm of low stress Si_3N_4 was deposited by low pressure chemical vapor deposition (LPCVD). On the back surface, the nitride was removed in a 400 μm x 400 μm square by optical lithography and reactive ion etching (RIE). The exposed silicon was etched in an orientation dependent anisotropic etchant (35% KOH solution at 85°C) through to the top surface, leaving a suspended 40 μm x 40 μm silicon nitride membrane. A single hole of size 30-50 nm was made through the membrane by electron beam lithography and RIE. Because of the strained geometry, the RIE rates were substantially reduced so that the far side opening was much smaller than actually patterned, thereby rendering the cross-section of a bowl-shaped geometry. A metallic gold contact of 200 nm thickness was evaporated onto the topside of the membrane, which filled the pore with gold. The sample was then immediately transferred into a solution of 2'-amino-4-ethynylphenyl-4'-ethynylphenyl-5'-nitro-1-(thioacetyl)benzene (0.5 mM in THF) and ammonium hydroxide (con. Aq., 5 μL per mg of 1-(thioacetyl)benzene) for the self-assembly to occur over a period of 48 hours, under an inert atmosphere of argon. The sample was then rinsed, quickly loaded into a vacuum chamber and mounted on a liquid nitrogen cooling stage for the bottom gold electron evaporation, in which 200 nm of gold was evaporated at 77K at a rate of less than 1 Å per second. The devices

were then diced into individual chips, bonded onto packaging sockets, and loaded into a variable temperature cryostat (Janis), and measured with a HP4145 Semiconductor Parameter Analyser.

A series of control experiments were done with alkanethiol-derived
5 conductive paths in SAM, using silicon-nitride membranes without pores, and
membranes with pores but without conductive paths. Both the gold-alkanethiolate-
gold, and the gold-silicon nitride membrane-gold junctions showed current levels at
the noise limit of the apparatus (less than 1 pA) for both bias polarities at both room
and low temperatures (60K). A device containing a SAM of conductive paths without
10 nitro or amine functionalities did not exhibit negative differential resistance behavior
under similar experimental conditions.

Fig. 8 is a plot of the $I(V)$ characteristics of a gold-(2'-amino-4-ethynylphenyl-
4'-ethynylphenyl-5'-nitro-1-benzenethiol)-gold molecular electronic device. The
measurement was made at 60 K. The current vs. voltage plot is fully reversible upon
15 change in bias sweep direction. Positive bias corresponds to hole injection in the thiol
end of the conductive path, electron injection from the evaporated contact end. The
peak to valley ratio (PVR) exceeds 10^3 . This performance exceeds that observed in
typical solid state quantum well resonant tunneling heterostructures. The intrinsic
PVR for such devices may be larger than that reported here due to typical leakage
20 currents in the silicon nitride.

Fig. 9 shows $I(V,T)$ characteristics of a Au-(2'-amino-4-ethynylphenyl-
4'-ethynylphenyl-5'-nitro-1-benzenethiolate)-Au device. This device exhibited peak
voltage position and current magnitude shifts with temperature, shown in Fig. 9.

25 Example 8: Observation of High-Conductivity Memory Effects in Molecular
Electronic Devices

The compound 2'-amino-4,4'-diphenylethynyl-5'-nitro-1-benzenethiolate was
incorporated into a gold contacted nanopore, as described in Example 7. An initially

low conductivity state was written into a high conductivity state upon application of a voltage pulse.

Fig. 10 shows the I(V) characteristics of a Au-(2'-amino-4,4'-diphenylethynyl-5'-nitro-1-benzenethiolate)-Au at 200 K, initially (defined as "0"), and after a write pulse (defined as "1"), and the difference between the two states (defined as "1"- "0"). These characteristics were measured under a low bias, high temperature regime. Positive bias corresponds to hole injection from the thiol-gold contact. The device initially probed with a positive voltage exhibits a low conductivity state. Subsequent positive sweeps show a high conductivity state with I(V) characteristics identical to the previous values ("1"). Device bias swept in the reverse bias direction causes the I(V) to be identically reset to the initial ("0" in this case) I(V) characteristic. The characteristics are repeatable to high accuracy, and device degradation is not observed.

Fig. 11 shows the difference characteristic ("1"- "0") of this system (Au-(2'-amino-4,4'-diphenylethynyl-5'-nitro-1-benzenethiolate)-Au) as a function of temperature. The peak current difference decreases approximately linearly with increasing temperature over the investigated range.

Example 9: Bit Retention Time

A characteristic bit retention time was obtained by measuring the stored high conductivity state at various time intervals after programming the Au-(2'-amino-4,4'-diphenylethynyl-5'-nitro-1-benzenethiolate)-Au device of Example 7. After an initial write bias sweep, the peak current of the stored state "1" exhibits an exponential decay with a time constant (τ) of 790 seconds at 260 K, as shown in Fig. 12. Measurements of the bit retention time at different temperatures yields an exponential dependence, with $1/T$, indicating an activated behavior as shown in Fig. 13. The behavior is described by $\tau = \tau_0 e^{(E_a/kT)}$. The activation energy over this bias regime was found to be approximately 76 ± 7 meV for this system.

Example 10: Observation of Low-Conductivity Memory Effects in Molecular Electronic Devices

The compound 4,4'-diphenylethynyl-2'-nitro-1-benzenethiolate was incorporated into a gold contacted nanopore, as described in Example 7. An initially high conductivity state was written into a low conductivity state upon application of a voltage pulse.

Fig. 14 shows the storage of this state in the system at 60 K. Fig. 15 shows this storage at 300 K. The window over which the "0" and "1" states differ by a constant amount of approximately 150 pA is nearly 5 volts, providing well separated thresholds. As described previously, subsequent read pulses and reset pulses identically recovered the I(V) characteristics. At 300 K, thermal activation does contribute some non-zero "0" current, although the thresholds are still well-separated (between 200 and 500 pA). The set points indicated (*ca.* 1.5 V and *ca.* 500 pA for "0", and *ca.* 1.5 V and *ca.* 100 pA for "1") are the operating points for the circuit described below in Example 11.

Example 11: Molecular Logic Diagram

Fig. 16 is a measured logic diagram demonstrating a random access memory (RAM) cell operating at ambient temperature using molecular scale electronic devices. The compound 4,4'-diphenylethynyl-2'-nitro-1-benzenethiolate was incorporated into a gold contacted nanopore, as described in Example 7. To convert the stored conductivity to standard voltage conventions, the output of the device was dropped across a resistor, sent to a comparator (set at the points diagrammed in Fig. 15, and inverted and gated with the read pulse. The upper trace shown in Fig. 16 is an input waveform applied to the device, and the lower trace is the RAM cell output. The first positive pulse configures the state of the cell by writing a bit, and the second and third positive pulses read the cell. The third pulse (and subsequent read pulses, not shown) demonstrates that the RAM cell is robust and continues to hold the state up to the limit of the bit retention time at this temperature. The negative pulse erases the bit, resetting the cell. The second set of four pulses

repeats this pattern, and many hours of continuous operation have been observed with no performance degradation.

Example 12: Observation of Room Temperature NDR

5 Fig. 17 is a plot of the I(V) characteristic of a gold-(4-ethynylphenyl-4'-ethynylphenyl-5'-nitro-1-benzenethiolate)-gold molecular electronic device at 300K. The peak to valley ratio (PVR) is smaller than that of the compound shown in Example 7, but NDR behavior persisted from low temperature.

 The device has a peak current density of greater than 16 A/cm^2 , and
10 NDR of less than $-144 \text{ m}\Omega\text{cm}^2$ and a PVR of $\sim 1.5:1$. Fig. 18 shows the I(V) characteristics of the same device at 190 K. The NDR peak is sharper, and the PVR is approximately 4:1. The reduction potential difference for this system is also roughly equal to the width of the I(V) peak.

Example 13: Cyclic Voltammetry of Molecular Scale Devices

 Cyclic voltammetry measurements of 4,4'-diphenylethynyl-5'-nitro-1-benzenethiolate were performed at room temperature on a BAS CV-50W voltametric analyzer using an Ag/AgNO₃ reference electrode, and solvent system of
15 dimethylformide and IM n-tetrabutylammoniumfloraborate with a scan rate of 100mV/sec. Fig. 19 shows the cyclic voltammetry reduction curve where the first and
20 the second reduction potential for compound 4,4'-diphenylethynyl-5'-nitro-1-benzenethiolate is 1.68 V and 2.33 respectively.

 Fig. 20 shows the cyclic voltammogram curve for 2'-amino-4,4'-diphenylethynyl-5'-nitro-benzenethiolate where the reduction potentials peaked at 1.4
25 V and 2.2 V respectively. The reduction potential difference is in approximate agreement with the width of the I(V) peak. The fact that 2'-amino-4,4'-diphenylethynyl-5'-nitro-benzenethiolate is more readily reduced than 4,4'-diphenylethynyl-5'-nitro-1-benzenethiolate (the reduction potential of 2'-amino-4,4'-diphenylethynyl-5'-nitro-benzenethiolate is 0.3 V less than that of 4,4'-

diphenylethynyl-5'-nitro-1-benzenethiolate could be responsible for the observation of room temperature NDR in 2'-amino-4,4'-diphenylethynyl-5'-nitro-benzenethiolate but not in 4,4'-diphenylethynyl-5'-nitro-1-benzenethiolate.

5 **Other Embodiments**

It is to be understood that while the invention has been described in conjunction with the detailed description thereof, the forgoing description is intended to illustrate and not limit the scope of the invention, which is defined by the scope of the appended claims. Other aspects, advantages, and modifications are within the
10 scope of the following claims.

What is claimed is:

1. An electronic device comprising:
at least two contacts; and
a monolayer of conductive organic material forming a conductive path between
5 said contacts, wherein said conductive path includes at least one electron withdrawing
group.
2. The device of claim 1, wherein said device exhibits high and low
conductivity states.
3. The device of claim 2, wherein said device is repeatedly switchable
10 between said high and said low conductivity states.
4. The device of claim 2, wherein said low conductivity state has a
current of less than about 100 pA.
5. The device of claim 4, wherein said low conductivity state has a
current of less than about 1 pA.
- 15 6. The device of claim 2, wherein said high conductivity state has a
current at least about 200 times higher than said low conductivity state.
7. The device of claim 6, wherein said high conductivity state has a
current at least about 500 times higher than said low conductivity state.
8. The device of claim 7, wherein said high conductivity state has a
20 current at least about 1000 times higher than said low conductivity state.
9. The device of claim 1, wherein said electron withdrawing group is
selected from the group consisting of cyano, isocyano, nitro, sulfonyl, β -carboxyvinyl,
sulfinyl, β,β -dicyanovinyl, halogenated alkyl, formyl, carboxyl, carbonyl,
alkyloxycarbonyl and aryloxycarbonyl, 1-tetrazolyl, 5-chloro-1-tetrazolyl, carbamoyl,
25 and sulfamoyl.
10. The device of claim 9, wherein said electron withdrawing group is
selected from the group consisting of cyano, isocyano and nitro.

11. The device of claim 1, wherein said electron withdrawing group is bonded to a phenyl ring in the conductive path.

12. The device of claim 1, further comprising at least one electron donating group.

5 13. The device of claim 1, wherein said conductive path comprises atoms, at least 70% of said atoms being sp - or sp^2 -hybridized atoms.

14. The device of claim 1, wherein said conductive path comprises alternating ethynyl and aryl groups.

10 15. The device of claim 14, wherein said conductive path comprises at least one phenyl-ethynyl linkage.

16. The device of claim 15, wherein at least one of said phenyl groups is substituted with an electron withdrawing group.

17. The device of claim 1, wherein said conductive path further comprises binding groups which bind said conductive path to said contacts.

15 18. The device of claim 17, wherein said binding groups are selected from the group consisting of sulfur atoms, oxygen atoms, cyano, carboxy, diazonium salt, halide, isocyano, phosphine, and tellurium and selenium atoms.

19. The device of claim 1, wherein said conductive path comprises biphenyl groups.

20 20. The device of claim 1, wherein said conductive path comprises ethenyl groups.

21. An electronic device comprising:
two contacts, wherein at least one contact is a palladium contact; and
a self-assembled monolayer of a conductive organic molecule comprising a
25 phenyl-ethynyl-substituted phenyl-ethynyl-phenyl linkage between said contacts,
wherein said substituted phenyl includes at least one nitro group, and wherein said
organic molecule is bonded to said palladium contact by at least one isocyano group
on a terminal phenyl of said linkage.

22. A memory circuit comprising:

- a) an input;
- b) an output;
- c) a molecular electronic device, said device comprising: at least two contacts;

5 and

a monolayer of conductive organic material forming a conductive path between said contacts, wherein said conductive path includes at least one electron withdrawing group, wherein one contact bridges said input and said output, and wherein another contact is grounded; and

- 10 d) a comparator bridging said input and said output, wherein said comparator is in electrical communication with a reference voltage.

23. A memory array comprising a plurality of memory circuits of claim 22, wherein said memory circuits are arranged in an addressable array.

- 24. A static random access memory cell comprising: at least a first and a
15 second molecular electronic device, each of said devices comprising: at least two contacts; and a monolayer of conductive organic material forming a conductive path between said contacts, wherein said conductive path includes at least one electron withdrawing group, wherein said first device has a contact connected to a reference voltage, and another contact connected to a node, wherein said second device has one
20 contact connected to ground, and another contact connected to said node, and wherein said node is further connected to ground.

25. The memory cell of claim 24, wherein said cell further comprises a gain component.

- 26. The device of claim 1, wherein the device exhibits negative differential
25 resistance at room temperature.

Fig. 1

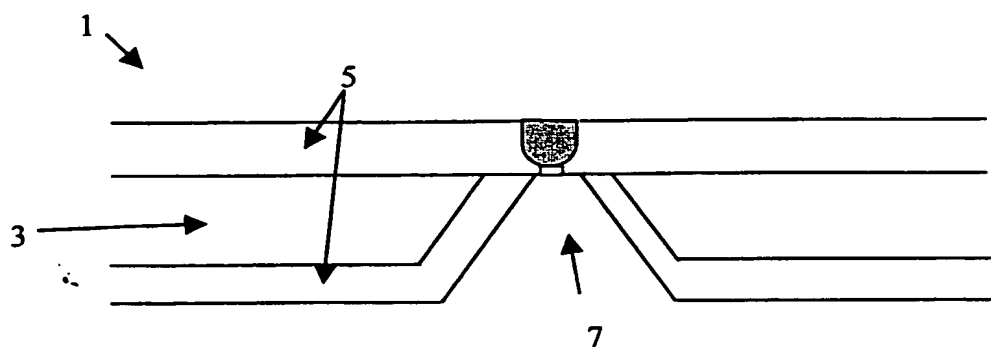


Fig. 2

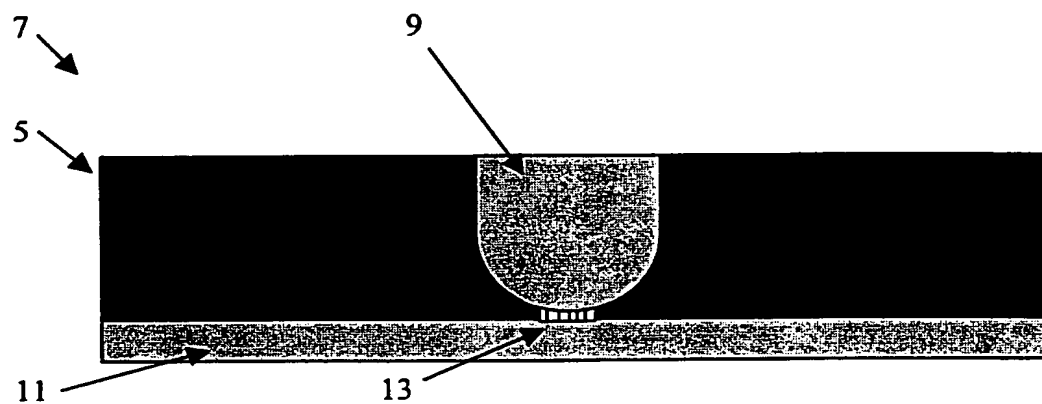


Fig. 3

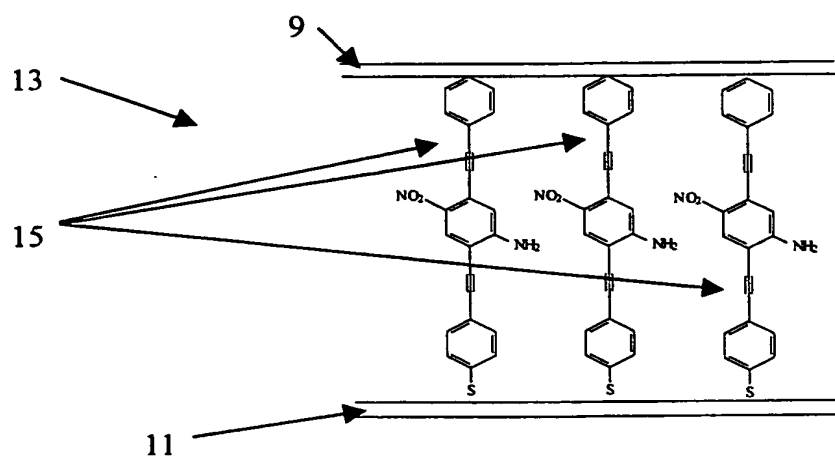


Fig. 4

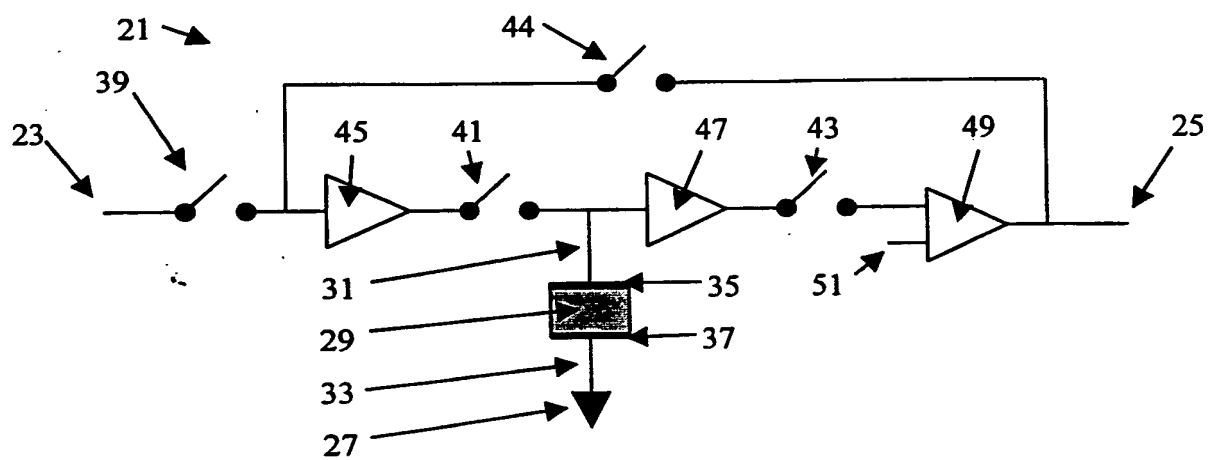


Fig. 5

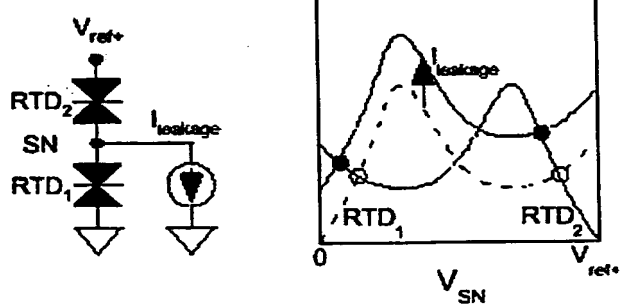


Fig. 6

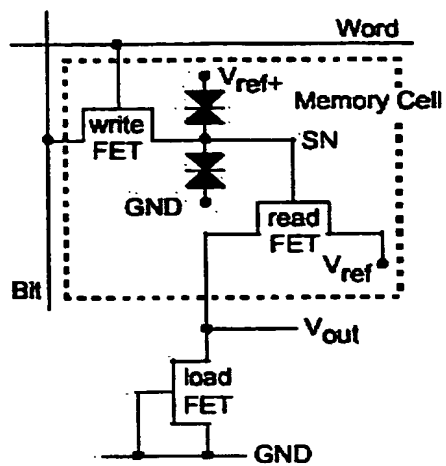


Fig. 7

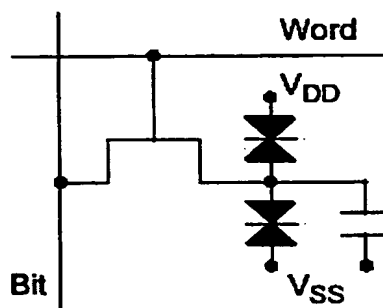


Fig. 8

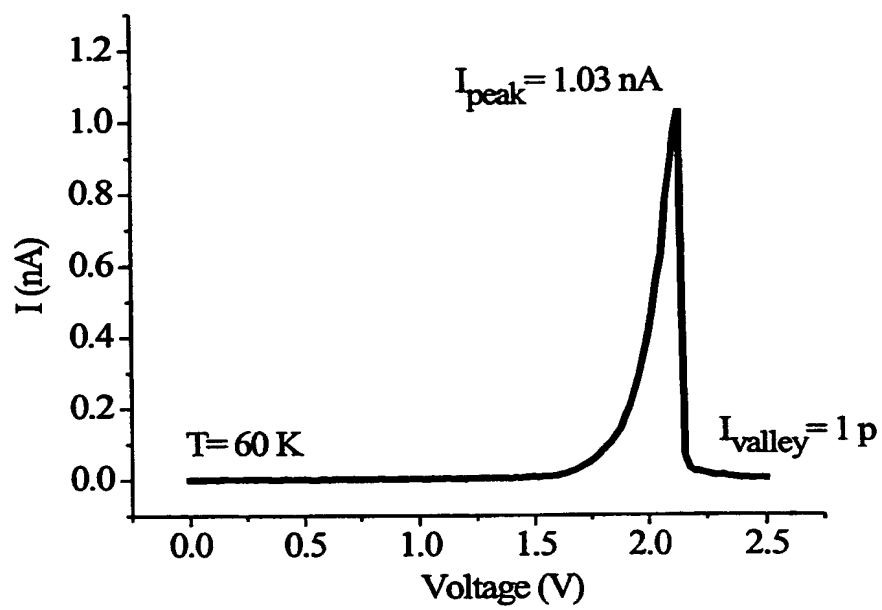


Fig. 9

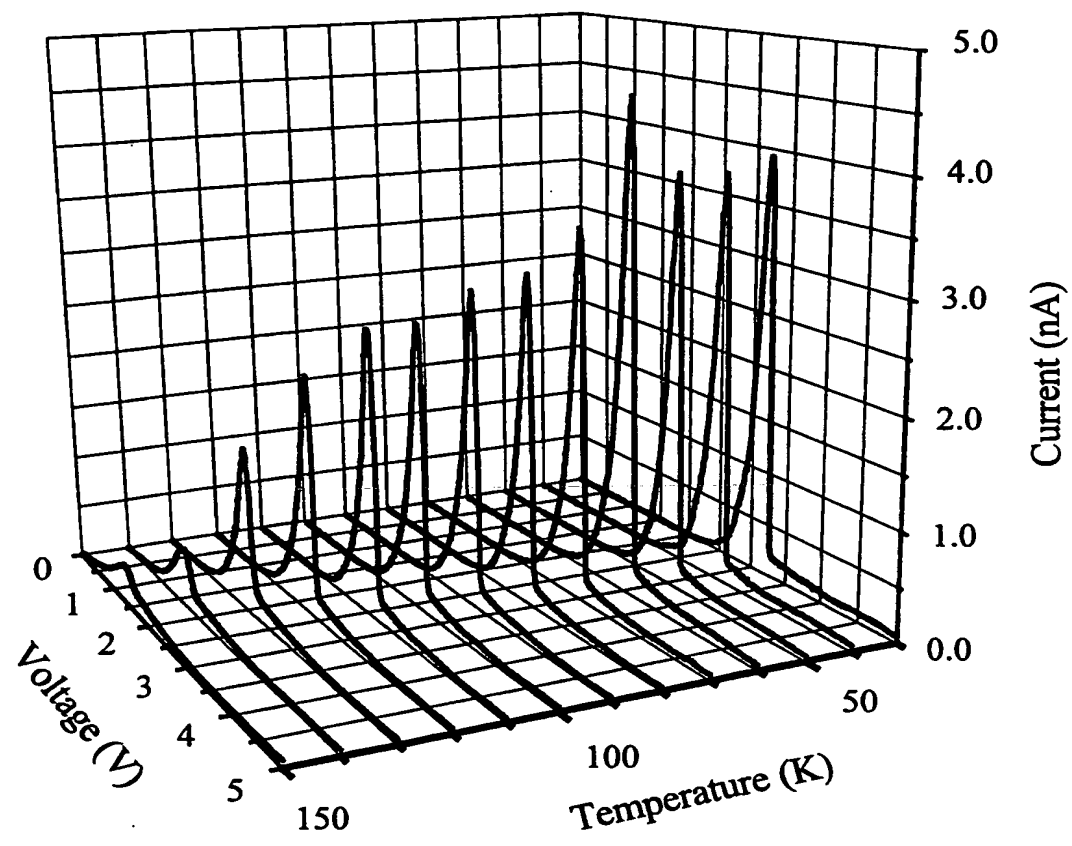


Fig. 10

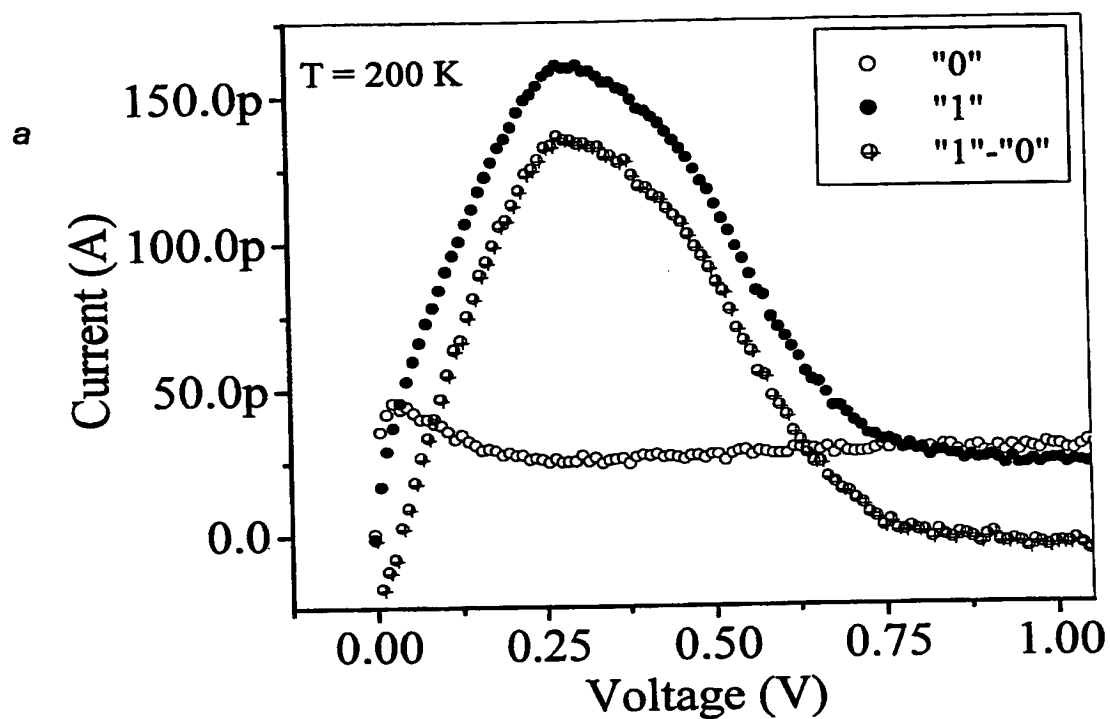


Fig. 11

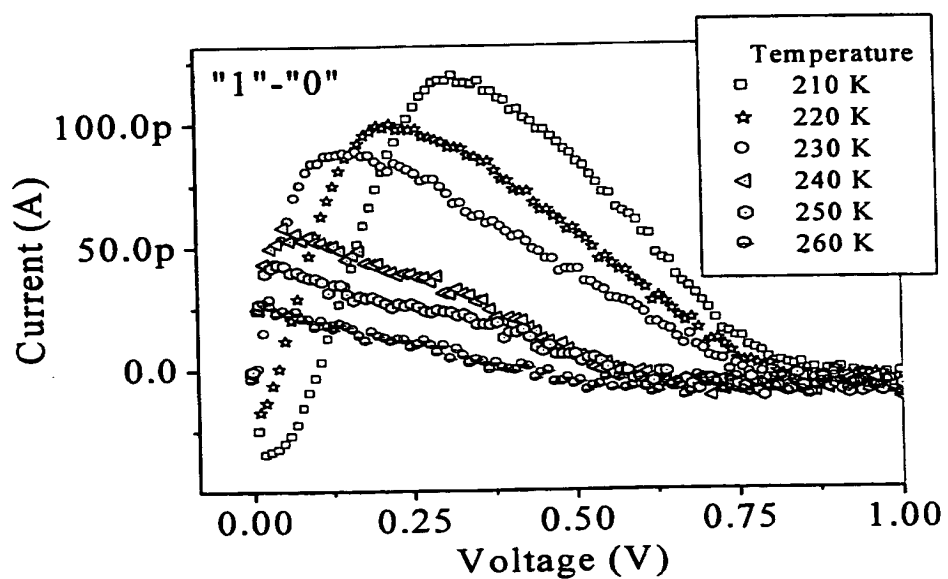


Fig. 12

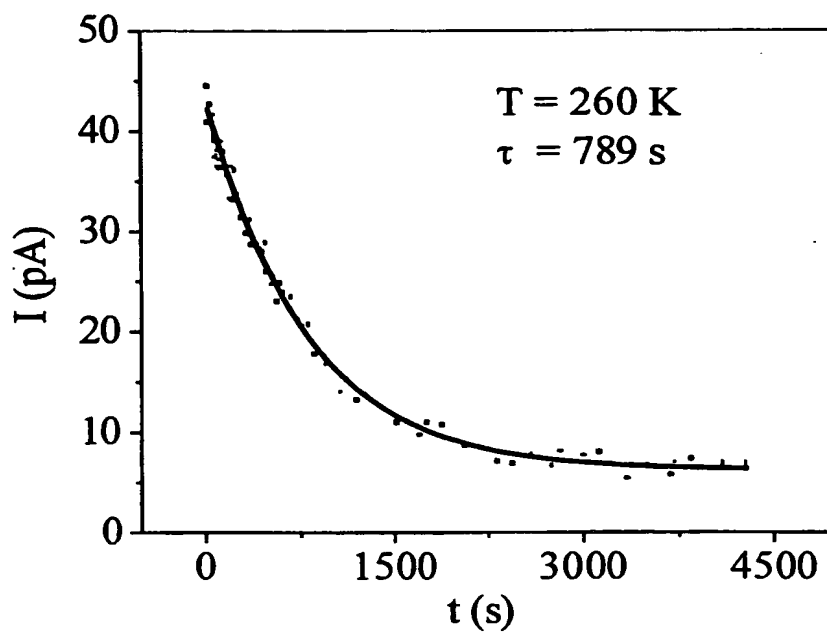


Fig. 13

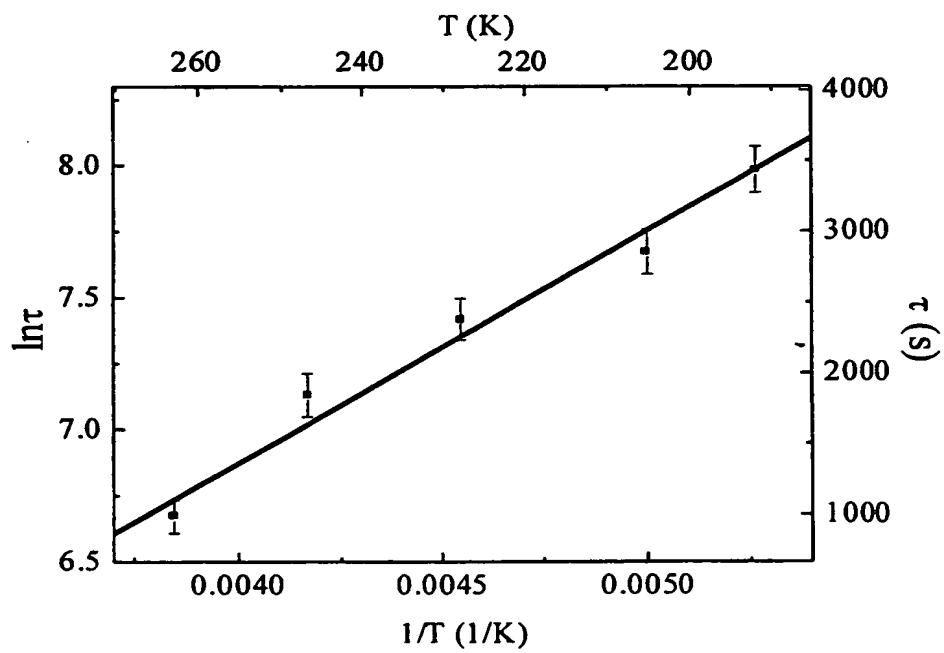


Fig. 14

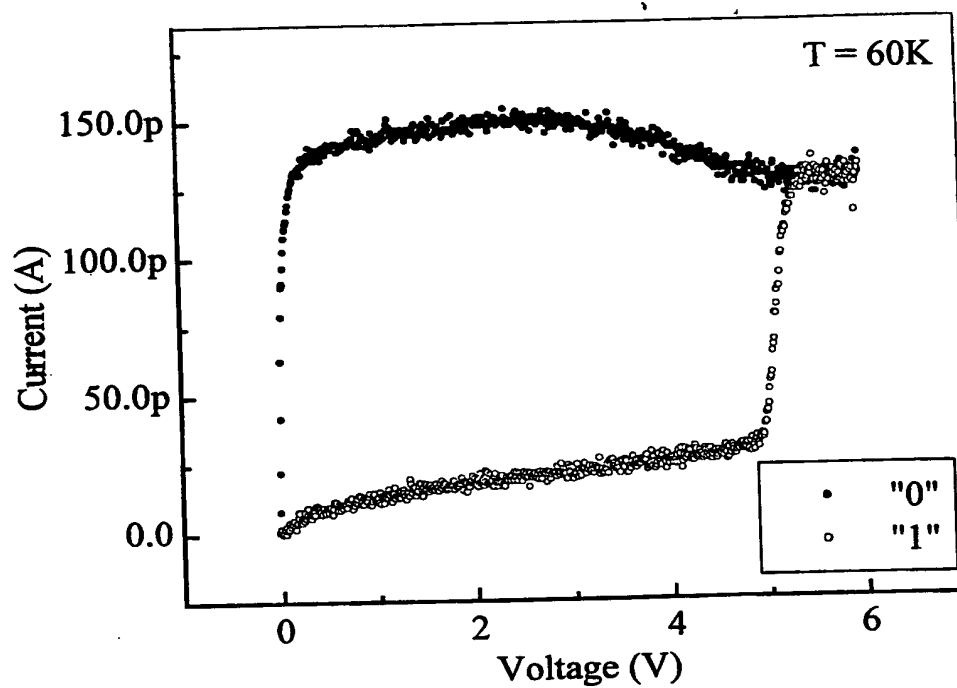


Fig. 15

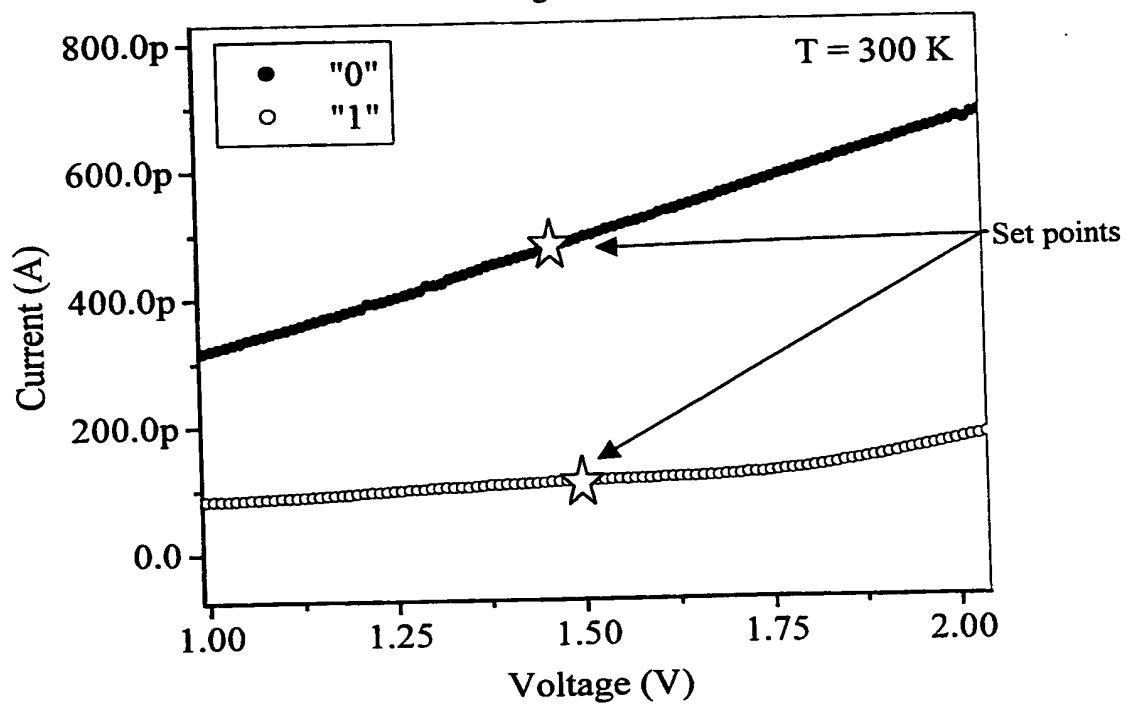


Fig. 16

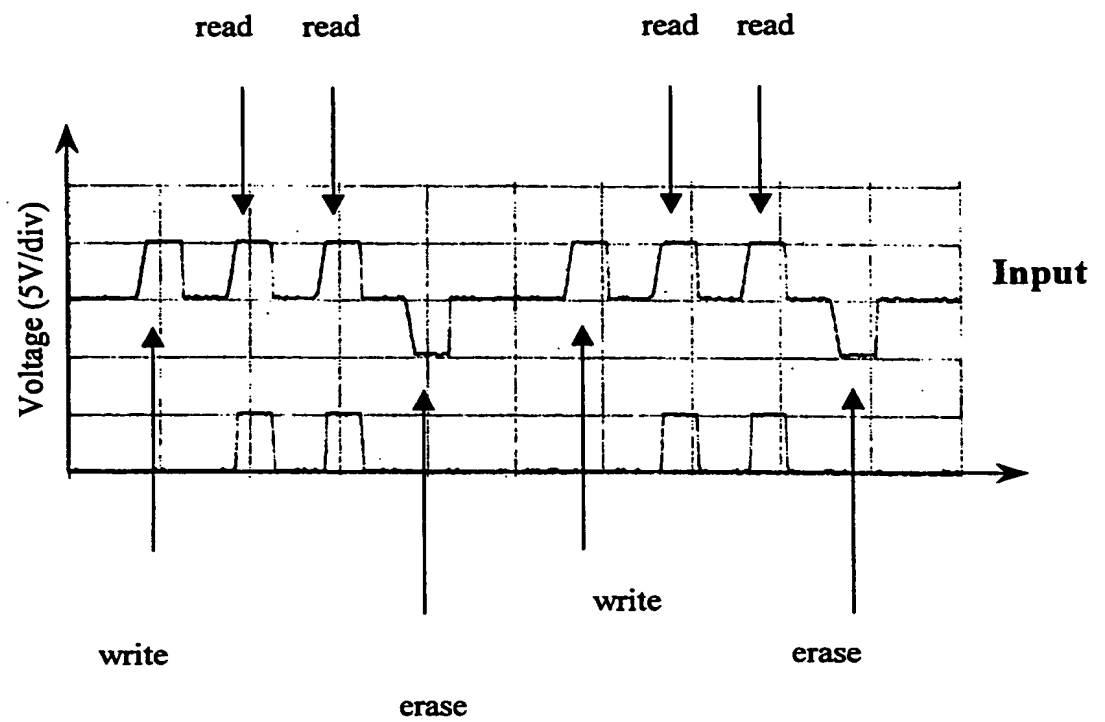


Fig. 17

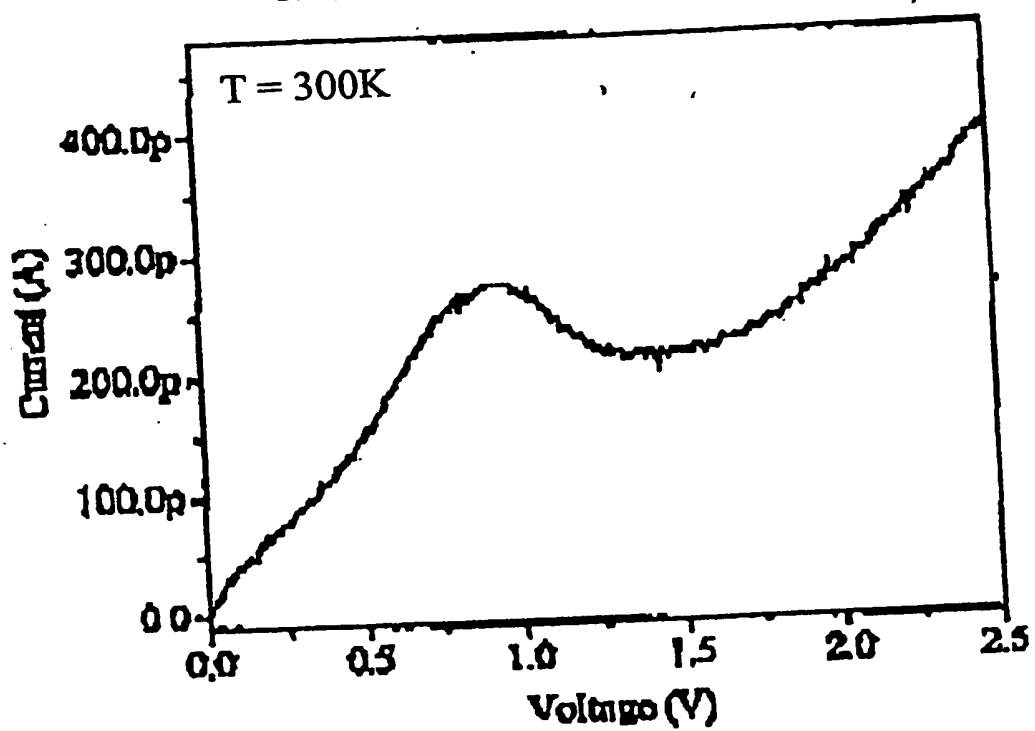


Fig. 18

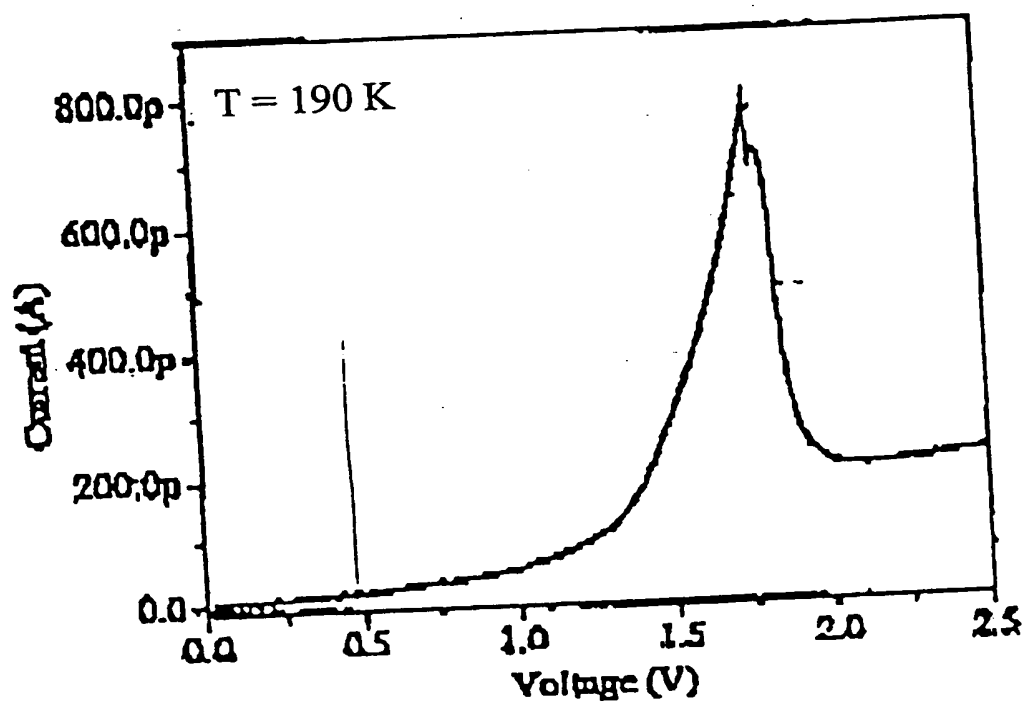


Fig. 19

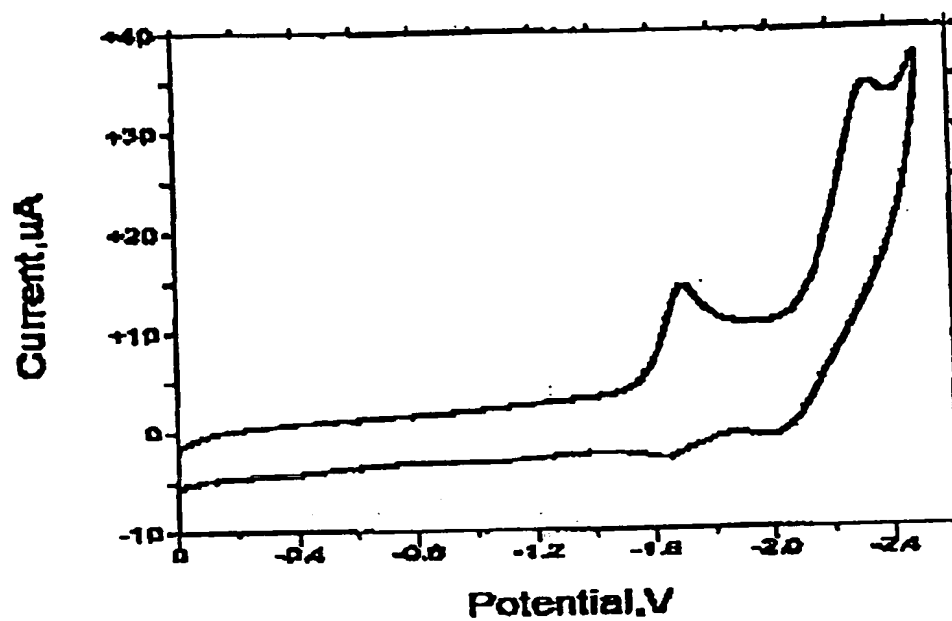
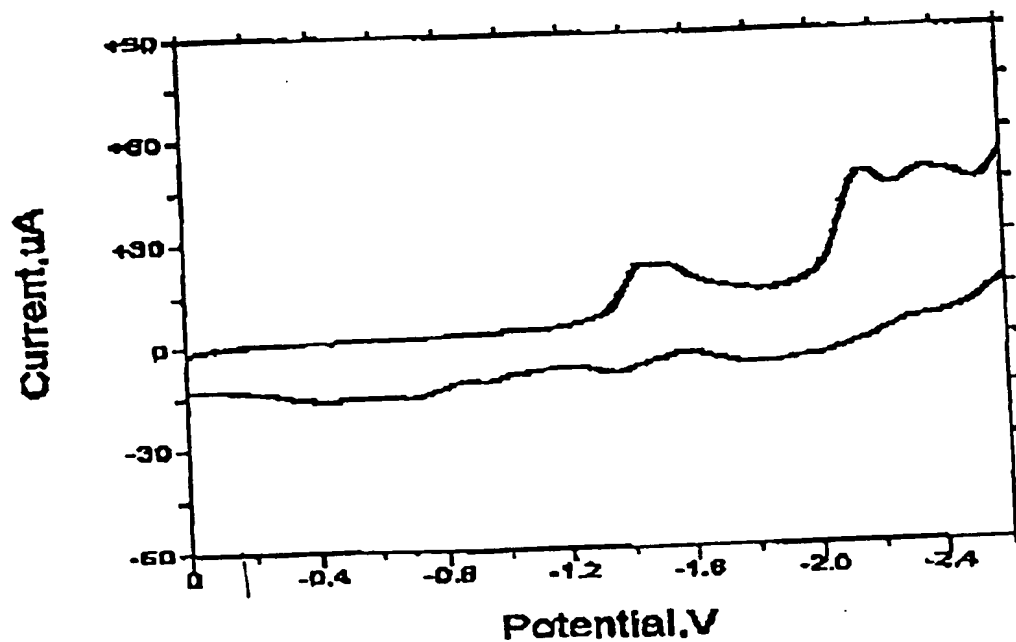


Fig. 20



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(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
19 April 2001 (19.04.2001)

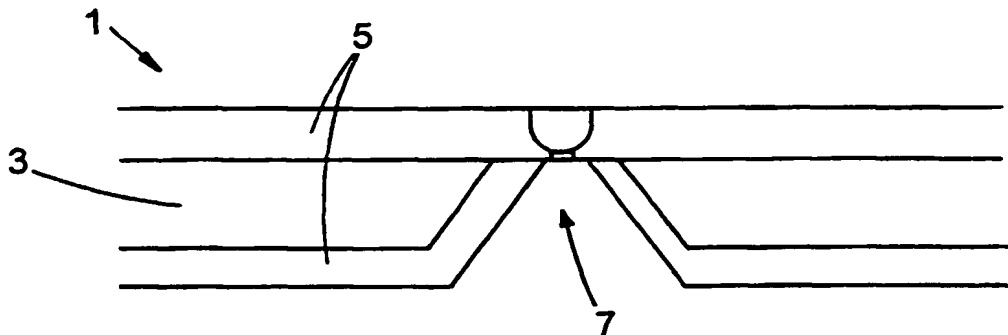
PCT

(10) International Publication Number
WO 01/27972 A3

- (51) International Patent Classification⁷: **B32B 27/32**,
H01L 35/24, C07D 207/30
- (21) International Application Number: PCT/US00/25518
- (22) International Filing Date:
18 September 2000 (18.09.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/154,716 20 September 1999 (20.09.1999) US
60/157,149 30 September 1999 (30.09.1999) US
09/527,885 20 March 2000 (20.03.2000) US
09/551,716 18 April 2000 (18.04.2000) US
- (63) Related by continuation (CON) or continuation-in-part (CIP) to earlier applications:
US 60/157,149 (CON)
Filed on 30 September 1999 (30.09.1999)
US 09/551,716 (CON)
Filed on 18 April 2000 (18.04.2000)
US 09/527,885 (CON)
Filed on 20 March 2000 (20.03.2000)
US 60/154,716 (CON)
Filed on 20 September 1999 (20.09.1999)
- (71) Applicant (for all designated States except US): **YALE UNIVERSITY** [US/US]; Yale Station, New Haven, CT 06520 (US).
- (72) Inventors; and
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- (74) Agent: **HEIBEL, George, E.**; Fish & Richardson P.C., Suite 2800, 45 Rockefeller Plaza, New York, NY 10111 (US).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report

[Continued on next page]

(54) Title: MOLECULAR SCALE ELECTRONIC DEVICES



(57) Abstract: Molecular scale electronic devices (1) are disclosed. Such devices include at least two conductive contacts (9 and 11), and a conductive path (13) bridging the contacts. The conductive path is able to be written into a perturbed state by a voltage pulse, which can be of high or low conductivity, relative to an initial state. The conductive path comprises organic molecules including at least one electron-withdrawing group. Room temperature negative differential resistance is exhibited by the devices.

WO 01/27972 A3



(88) Date of publication of the international search report:
22 November 2001

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

INTERNATIONAL SEARCH REPORT

 International application No.
 PCT/US00/25518

A. CLASSIFICATION OF SUBJECT MATTER IPC(7) : B32B 27/32; H01L 35/24; C07D 207/30 US CL : 428/215; 257/40; 548/562 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 428/215; 257/40; 548/562		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched none		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EAST		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,814,833 A (JENEKHE) 29 SEPTEMBER 1998, (29/09/98) entire document,	1-21 and 26
Y	US 4,629,798 A (TRAYNOR) 16 December 1986 (16/12/86) entire document.	1-21 and 26
A	US 5,110,669 A (KNOBEL ET AL.) 05 May 1992 (05/05/92) entire document.	1-21, 26
A	US 5,563,424 A (YANG ET AL.) 08 October 1996 (08/10/96) entire document	1-21, 26
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art *G* document member of the same patent family	
A document defining the general state of the art which is not considered to be of particular relevance *E* earlier document published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 23 APRIL 2001	Date of mailing of the international search report 10 MAY 2001	
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer Y. TRONG PHAN <i>[Signature]</i> Telephone No. (703) 308-4870	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/25518

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-21 and 26

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/25518

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

Group I, claim(s) 1-22, 26 drawn to an electronic device.

Group II, claim(s) 22-25, drawn to a memory device.

The inventions listed as Groups I and II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reason: they are unrelated inventions which have different modes of operation, different functions and different effects.

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